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UNIVERSITÉ DE MONTRÉAL

PERFORMANCE OF AGED PAC SUSPENSIONS IN A HYBRID MEMBRANE PROCESS FOR DRINKING WATER PRODUCTION

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Cette thèse intitulée:

PERFORMANCE OF AGED PAC SUSPENSIONS IN A HYBRID MEMBRANE PROCESS FOR DRINKING WATER PRODUCTION

présentée par : STOQUART Céline

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a été dûment acceptée par le jury d'examen constitué de :

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DEDICATION

To Fredy, my grandfather,

Who values hard work and education above all.

A map of the world that does not include Utopia is not worth even glancing at, for it leaves out the one country at which Humanity is always landing. And when Humanity lands there, it looks out, and, seeing a better country, sets sail. Progress is the realization of Utopias.

O. Wilde

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RÉSUMÉ

Les procédés membranaires hybrides (PMHs) allient l'usage de la filtration membranaire basse pression permettant l'enlèvement efficace des particules, y celui compris de parasites comme *Cryptosporidium,* à l'usage du charbon actif en poudre (CAP) pour le traitement de la contamination dissoute. Les PMHs sont une alternative prometteuse à la chaine de traitement conventionnelle, qui ne permet plus actuellement aux usines de production d'eau potable de rencontrer les normes de plus en plus sévères sur les composés dissous. Afin de diminuer les coûts opérationnels du procédé, il a été proposé de laisser vieillir le CAP dans le PMH et donc de minimiser le dosage de CAP frais. Jusqu'à présent, des études à l'échelle pilote ont mis en évidence le potentiel du PMH pour l'enlèvement de l'azote ammoniacal et du carbone organique dissous (COD) lorsqu'opéré avec de hauts temps de rétention de CAP (CAP âgé). Par contre, son potentiel à enlever les micropolluants, actuellement au centre des préoccupations des usines de traitement, reste inconnu. Il a été suggéré que l'activité bactérienne contribue de façon majeure à l'enlèvement des composés dissous lorsque l'âge du CAP est élevé (>7 jours). L'adsorption des composés dissous ne peut néanmoins être complètement écartée. Toutefois, les rôles respectifs de ces deux mécanismes pour l'enlèvement des composés dissous par le CAP âgé n'ont jamais été différenciés. Finalement, alors que l'adsorption et l'activité biologique sont deux mécanismes sensibles à la température, le potentiel du PMH en eau froide est peu connu. En conséquence, la disponibilité limitée d'information nuit à la pleine compréhension du procédé, conduisant à une opération non-optimisée du contacteur à CAP âgé dans le PMH.

Le principal objectif de ce projet de recherche est de décrire la performance du contacteur à CAP du PMH pour l'enlèvement de l'azote ammoniacal, du COD, du COD biodégradable (CODB) et des micropolluants. Dans ce projet, l'emphase est mise sur l'opération du PMH avec de hauts temps de rétention de CAP. Plus spécifiquement, les objectifs sont de (1) développer et comparer des méthodes permettant de quantifier la biomasse développée sur le CAP âgé, (2) développer une méthode permettant de produire un témoin abiotique à partir de CAP colonisé, (3) caractériser les cinétiques d'enlèvement de l'azote ammoniacal, du COD, du CODB et de micropolluants dans le contacteur à CAP du PMH, (4) évaluer l'impact de la température sur la performance du contacteur à CAP d'un PMH, (5) déterminer quelle est l'importance relative de l'adsorption et de l'activité biologique comme mécanismes responsables de l'enlèvement de

l'azote ammoniacal, du COD et des micropolluants dans le contacteur à CAP d'un PMH, et (6) différencier l'importance du temps de rétention hydraulique (TRH), de l'âge du CAP et de la concentration de CAP comme paramètres clefs pour l'optimisation de la performance du contacteur à CAP d'un PMH.

La première phase de travail de ce doctorat a consisté en une série de développements méthodologiques, formant la base nécessaire à l'étude du CAP âgé. Ces méthodes ont pour objectifs i) la quantification de la biomasse hétérotrophe et nitrifiante colonisant le CAP âgé et ii) la production de témoins abiotiques à partir d'échantillons de CAP colonisé. Ces témoins abiotiques sont en effet nécessaires à l'atteinte de l'objectif spécifique #5. Au cours de ce projet, plusieurs des méthodes de quantification de biomasse hétérotrophe et nitrifiante développées pour le charbon actif en grain (CAG) ont été adaptées au CAP. En outre, une méthode originale est proposée, le taux de consommation d'acétate (PAU), afin de réduire les problèmes logistiques et budgétaires associés à l'utilisation de ^{14}C-glucose lors de la mesure du taux de respiration du glucose potentiel (PGR), basant la quantification de la biomasse hétérotrophe active sur la consommation de glucose marqué. Les quantifications réalisées ont révélé une densité de biomasse bactérienne hétérotrophe et nitrifiante sur CAP de 10 et de 60 jours (par g sec de CAP) comparable à celle mesurée sur du CAG échantillonné en surface de filtres biologiques. L'irradiation aux rayons gamma est la méthode choisie pour produire des témoins abiotiques de CAP colonisé. Une dose optimale de rayons gamma a été recommandée sur base de cinétiques d'adsorption de bleu de méthylène et de comptages bactériens sur gélose. Les cinétiques d'adsorption du COD réfractaire (CODR) sur le CAP irradié à la dose optimisée ont confirmé que les caractéristiques d'adsorption du CAP colonisé n'avaient pas été altérées par l'irradiation. L'irradiation à la dose optimisée a, en outre, réduit l'activité hétérotrophe bactérienne (exprimée en PGR) de 83%. La méthode par irradiation aux rayons gamma s'est donc révélée efficace pour inhiber l'activité bactérienne hétérotrophe et ce, sans modifier significativement les caractéristiques d'adsorption du CAP colonisé.

La seconde partie de cette étude s'est concentrée sur la démonstration de l'efficacité du PMH pour l'enlèvement de l'azote ammoniacal, du COD, ainsi que d'un mélange de micropolluants. Premièrement, l'enlèvement d'azote ammoniacal au sein du contacteur à CAP du PMH a été simulé en laboratoire en présence de trois concentrations de CAP (environ 1, 5 et 10 g/L), de trois âges de CAP (0, 10 et 60 jours), sous deux conditions de température contrastées (7 et 22°C) et

ce, dans deux matrices d'eau décantée (naturelle avec 100 µgN-NH_4/L et dosée à environ 1000 µgN-NH_4/L). Sous les conditions opératoires au pilote (5 et 10 g PAC/L), la colonisation du CAP par les bactéries nitrifiantes ne semble pas avoir été limitée par l'espace disponible. Par conséquent, la concentration en CAP ne s'est pas révélée être un paramètre d'opération clef pour l'enlèvement de l'azote ammoniacal à condition que suffisamment de support soit présent pour la croissance de la biomasse. Au contraire, la quantité d'azote ammoniacal s'est révélée limitante pour la croissance bactérienne (TRH de 67 min). Par ailleurs, le CAP de 60 jours s'est révélé plus efficace à 7°C (78% d'enlèvement) que le CAP de 10 jours (<10%). L'activité bactérienne et l'adsorption de l'azote ammoniacal se sont toutes deux révélées supérieures sur le CAP de 60 jours que sur celui de 10 jours. Il est suggéré que l'adsorption de l'azote ammoniacal dans le réacteur à CAP de 60 jours ait lieu à la fois sur le CAP lui-même, mais aussi sur les matières en suspension accumulées dans le réacteur. En cas de pic de pollution dans l'eau brute (1000 µgN-NH_4/L), un enlèvement de 50 % sur CAP de 10 et 60 jours a été maintenu grâce à un mélange d'adsorption et de nitrification à 22°C. Une limitation par le phosphate est suggérée comme responsable que la faible activité biologique nitrifiante observée mais partiellement compensée par l'adsorption. Un modèle original basé sur les cinétiques d'enlèvement de l'azote ammoniacal a été développé. Ce modèle prédictif a permis de déterminer l'importance relative de l'adsorption et de la nitrification pour l'enlèvement de l'azote ammoniacal dans les contacteurs à CAP colonisé dans les conditions testées.

Deuxièmement, des simulations en laboratoire ont été effectuées pour caractériser l'enlèvement du COD, du CODB et du CODR. Une approche similaire à celle employée pour le suivi de l'azote ammoniacal a été utilisée, et des conditions opératoires (âge, concentration et température) identiques ont été appliquées dans une matrice d'eau décantée et d'eau brute pré-ozonée (0 à 1.5 g O_3/gC) ou non. La comparaison des cinétiques entres les CAPs colonisés et leurs contrôles abiotiques respectifs a démontré que, dans les conditions testées, la biodégradation ne contribue que de façon marginale à l'enlèvement du COD. L'adsorption du COD, favorisée à 22°C, s'est révélée être le mécanisme principal de traitement. Un modèle original, intégrant la distribution d'âge dans les suspensions de CAP âgé, décrit la performance des contacteurs à CAP opérés à l'équilibre avec des âges de CAP élevés. Ce modèle montre qu'en présence d'une suspension de CAP de 60 jours, c'est la fraction de CAP la plus jeune (25 jours et moins, correspondant à 34% de la masse totale de charbon) qui est responsable de 80%

de l'enlèvement de COD. Lors de l'utilisation d'une matrice présentant une concentration initiale en COD plus élevée (eau brute) ou une affinité plus faible pour le CAP (eau décantée pré-ozonée), le modèle montre que la capacité d'adsorption résiduelle des fractions de CAP plus âgées intervient dans l'enlèvement du COD.

Finalement, un mélange de micropolluants (atrazine, déethylatrazine (DEA), linuron, microcystine, caféine, carbamazépine, sulfaméthoxazole, diclofénac, progestérone et médroxyprogestérone) a été dosé dans de l'eau décantée (0 et 0.85 gO_3/gC) à des concentrations représentatives des concentrations d'eau de surface (de 130 ng/L à 33 µg/L). Les cinétiques d'enlèvement de chacun de ces composés ont été suivies sur une période de 7h à 48h en présence de 1 g/L de CAP de 0, 10, 60 jours et 60 jours irradié aux rayons gamma. Même en présence de matière organique naturelle, les micropolluants dosés dans la matrice ont rapidement été adsorbés par le CAP. Aucune biodégradation n'a été mise en évidence. Ainsi, 95% de chacun des composés ont été adsorbés en moins de 5 min. La compétition directe avec la matière organique n'a pas influencé l'efficacité du procédé pour les composés dosés à des concentrations représentatives de celles rencontrées dans l'environnement. Par conséquent, le PMH opéré pour l'enlèvement d'azote ammoniacal et de COD semble efficace pour le contrôle d'évènements transitoires de pollutions en micropolluants lorsque les recommandations de l'Organisation Mondiale de la Santé sont visées (atrazine: 2 µg/L et microcystine : 1 µg/L). Cependant, les conditions opératoires appliquées n'ont pas permis de rencontrer la règlementation européenne pour l'atrazine et le DEA (0.1 µg/L), qui nécessiterait une optimisation spécifique à cet objectif de traitement.

De manière générale, les travaux réalisés au cours de ce doctorat ont mis en évidence le rôle de l'adsorption résiduelle pour l'enlèvement des composés dissous par des suspensions de CAP de 10 et de 60 jours. Les résultats obtenus pour l'enlèvement de micropolluants sont prometteurs, mais des recherches supplémentaires sont requises pour confirmer l'efficacité du procédé sous des conditions plus variées. Le travail de modélisation réalisé au cours de ce projet a permis de mieux comprendre le fonctionnement des suspensions de CAP âgé. Les travaux de ce doctorat contribuent de façon originale à l'optimisation de l'opération des PMHs. L'optimisation des paramètres d'opération du procédé variera avec la qualité de l'eau à traiter ainsi qu'avec les objectifs de traitement fixés. La concentration, l'âge de CAP ainsi que le TRH sont inter-reliés, il est donc recommandé d'optimiser l'opération des PMHs en effectuant des essais pilotes et de

tenir compte des variabilités de qualité de l'eau à traiter. De manière générale, lorsque l'activité biologique est nécessaire pour atteindre les objectifs de traitement fixés, il est recommandé d'appliquer un TRH de 15 min au minimum. Par contre, de plus faibles TRH pourraient être appliqués si l'adsorption est le mécanisme principal du procédé. Le TRH ayant un impact significatif sur le coût du procédé, il est recommandé que les prochains efforts de recherche se concentrent sur l'optimisation du mélange du contacteur à charbon.

ABSTRACT

Hybrid membrane processes (HMPs) couple membrane filtration with powdered activated carbon (PAC). In HMPs, low-pressure membranes ensure an efficient particle removal, including protozoan parasites such as *Cryptosporidium*, while the PAC contactor is devoted to the removal of dissolved compounds. Such processes are emerging as a promising alternative to conventional treatment chains, which no longer allow the drinking water facilities to comply with increasingly stringent regulations on the treated water quality. To decrease the operating costs associated with virgin PAC consumption, it was suggested to let the PAC age in the PAC contactor of the process. Until now, the potential of using aged PAC in HMPs has been demonstrated for ammonia and DOC removal, but the potential to remove micropollutants remains unknown. It is suggested that the biological activity in aged PAC contactors contributes significantly to the removal of the dissolved compounds. Yet, neither the extent of the biomass on the aged PAC, nor the residual adsorption capacity, was quantified. No study focused on discriminating the mechanisms responsible for the treatment when using aged PAC suspensions. Most of the data published on HMPs using aged PAC were gathered at pilot scale under warm water conditions, yet the efficiency of the process is most likely sensitive to temperature changes. There is currently little information available on the efficiency of HMPs under cold water conditions. This lack of information hinders the optimization of the HMP, leading to sub-optimal usage of aged PAC.

The main objective of this research project is to describe the performance of the PAC contactor of HMPs in removing ammonia, dissolved organic carbon (DOC), biodegradable DOC (BDOC) and micropollutants. In particular, emphasis was placed on the operation of the HMP under high PAC residence times. On a more detailed level, the objectives of this project were (1) to develop and compare methods to quantify the biomass developed on aged PAC, (2) to develop a method to produce an abiotic control for aged PAC, (3) to characterize the removal kinetics of ammonia, DOC, BDOC and micropollutants occurring in the carbon contactor of an HMP, (4) to evaluate the impact of water temperature on the performance of the carbon contactor of an HMP, (5) to discriminate the relative importance of adsorption versus biological oxidation as mechanisms responsible for ammonia, DOC and micropollutants removal in the PAC contactor of an HMP, and finally (6) to differentiate the relative importance of the hydraulic retention time (HRT), the

PAC age and the PAC concentration as key operating parameters on the optimization of the performance of the PAC contactor of an HMP.

To set the basis on the study of aged PACs, the first part of this research project consisted in methodological developments i) to quantify the heterotrophic and nitrifying biomass colonizing aged PAC, and ii) to create a reliable abiotic control of the colonized PAC, which is required for discriminating the mechanisms occurring on aged PAC. Heterotrophic and nitrifying biomass quantifying methods developed for colonized granular activated carbon (GAC) were successfully adapted to the aged PAC. The preferred methods were the potential ^{14}C-glucose respiration (PGR) rate and the potential nitrifying activity (PNA), as they quantify the active heterotrophic and nitrifying biomass, which is most likely responsible for the depletion of BDOC and ammonia. An alternative method to the PGR, the potential acetate uptake (PAU) rate, was developed to alleviate the logistical and budgetary issues associated with the utilization of radio-labeled glucose. The densities (per gram of dry PAC) of both active heterotrophic and nitrifying biomasses were found comparable to that of the GAC sampled from the surface of a biological GAC filter. The gamma-irradiation was demonstrated as a reliable method to produce abiotic samples from soils, and was therefore chosen to produce abiotic colonized PAC samples in this project. In order to determine the optimized dosage of gamma-rays, increased doses were applied on PAC samples. Heterotrophic plate counts and methylene blue adsorption kinetics were used to determine respectively the lowest gamma ray dose required to inhibit the bacterial activity, and the highest dose that could be applied without affecting the aged PAC adsorption capacity and kinetics. Refractory DOC (RDOC) adsorption kinetics confirmed the accuracy of the dose chosen as the adsorptive behavior of the aged PAC was not affected. PGR rates were decreased 83% at the optimized dose. The gamma-irradiation method was therefore proven efficient and used in the following work phases of this research.

The second part of this study focused on the removal of ammonia, DOC and a mixture of micropollutants. Firstly, the PAC contactor of an HMP was simulated at lab-scale to monitor ammonia removal kinetics. Three PAC concentrations (approximately 1-5-10 g/L) of three PAC ages (0-10-60 days) were tested at two temperatures (7-22°C), in settled water with ambient influent condition (100 µg $N–NH_4$/L) as well as under a simulated peak pollution scenario (1000 µg $N–NH_4$/L). The kinetics evidenced that ammonia flux at pilot scale limited biomass growth (HRT = 67 min). In contrast, PAC colonization was not limited by the available surface and thus,

PAC concentration was not a key operating parameter under the colonizing conditions tested (5-10 g/L). Ammonia adsorption was significant onto virgin PAC but the ammonia nitrification was crucial to reach complete ammonia removal at 22°C. When using colonized PAC, the 60-d PAC offered a better resilience to temperature decreases (78% at 7°C) as well as lower operating costs than the 10-d PAC (<10% at 7°C). Significant ammonia adsorption was also evidenced on 60-d PAC suspension, most probably due to PAC and the presence of suspended solids, but not on 10-d PAC. Adsorption and nitrifying activity were superior on 60-d PAC than on 10-d PAC at 7°C. In case of peak pollution, the process was most probably phosphate-limited but a mixed adsorption/nitrification still allowed 50% ammonia removal on 10-d and 60-d PAC at 22°C. A kinetics based model was developed to predict ammonia removals and to determine the relative importance of the adsorption and nitrification on colonized PAC under the conditions tested.

DOC, BDOC and RDOC removals occurring in the PAC contactor of an HMP were also simulated at lab-scale. Similar conditions to that of the ammonia removal kinetics were tested. The initial ammonia concentration remained untouched in the water matrices (settled water and raw water) but the BDOC-to-DOC ratio was altered by pre-ozonation (0 to 1.5 g O_3/g C). The 10-d and 60-d abiotic controls were used to discriminate DOC adsorption from biodegradation. DOC biodegradation contributed marginally to DOC removal in the investigated conditions and DOC adsorption was increased at higher temperature. An original model integrating the PAC age distribution was developed to predict DOC removal in aged PAC contactors operated at steady-state. At a mean PAC residence time of 60-d, the younger PAC fraction (25-d and less) was primarily responsible for DOC adsorption (> 80%). This fraction represents 34% of the mass of PAC in the contactor. When using a water matrix with a higher initial DOC concentration (raw water) or a lower affinity for PAC (pre-ozonated settled water), the residual adsorption capacity of that older fraction was proven useful.

Lastly, a mixture of micropollutants (atrazine, deethylatrazine (DEA), linuron, microcystin, caffeine, carbamazepine, sulfamethoxazole, diclofenac, progesterone and medroxyprogesterone) was spiked at environmentally relevant concentrations (from 130 ng/L to 33 µg/L) in settled water (0 and 0.85 gO_3/gC). The micropollutants concentration depletion was monitored over a period of 7h to 48 h on 1 g/L of 0-d, 10-d, 60-d PAC and gamma-irradiated 60-d PAC. Even in presence of NOM, the spiked micropollutants were rapidly adsorbed on aged PAC. No biodegradation was observed. Removals superior to 95% were reached within 5 minutes, and

direct competition with NOM did not impact the efficiency of the process when micropollutants were spiked at environmentally relevant concentrations. Therefore, HMPs operated to remove DOC and ammonia can control transient micropollutant pollution and comply with the World health Organization recommendations for atrazine (2 µg/L) and microcystin (1 µg/L). However, the stricter European regulations for atrazine and DEA (0.1 µg/L) could not be met with 10-d and 60-d PAC under the operating conditions tested. Reaching such strict treatment objective would require a specific optimization of the process.

In general, this PhD research evidenced the role of the residual adsorption of aged PAC suspensions for the treatment of dissolved compounds. From the results obtained in this project, the potential of HMPs using aged PAC to remove micropollutants was evidenced. Additional research is however required to validate this potential under varied operating conditions. The modeling work improved the understanding of aged PACs. Finally, this research work provides original information on the optimization of HMPs. The optimization of the operating parameters will vary with the water quality targeted and the quality of the influent water. The PAC concentration, PAC age and HRT are inter-related. Therefore, it is recommended to optimize the operation of HMPs at pilot scale. Seasonal variations should be accounted for. An HRT of at least 15 min is required when the biological activity is mandatory to reach the water quality objectives. Lower HRT might be applied if adsorption is favored. Finally, as the HRT has a strong impact on the total cost of the process (capital and operational expenditure), PAC contactors' hydraulic should be the point of focus of future research.

CONDENSÉ EN FRANÇAIS

Les procédés membranaires hybrides (PMH) allient l'usage de la filtration membranaire à celui du charbon actif en poudre (CAP). Dans les PMHs, les membranes à basse pression assurent un enlèvement efficace des particules, incluant les protozoaires parasites comme *Cryptosporidium*, tandis que le CAP est employé pour l'enlèvement des composés dissous. Les procédés tels que le PMH se présentent de plus en plus comme une alternative prometteuse à la chaine de traitement conventionnelle constituée de la coagulation, floculation, de la décantation et de la filtration. En effet, la chaine de traitement conventionnelle ne permet plus actuellement aux usines de production d'eau potable de rencontrer les normes de plus en plus strictes concernant la pollution dissoute. Actuellement, les usines équipées de PMHs sont associées à l'utilisation de CAP neuf. C'est particulièrement le cas en Europe, où les normes sur les concentrations en micropolluants dans l'eau potable sont extrêmement sévères (0.1 µg/L pour chaque pesticide, avec une concentration maximale tolérée de 0.5 µg/L). Cependant, l'opération du PMH avec de faibles temps de résidence de CAP implique des coûts opérationnels très élevés, coûts qui peuvent freiner l'installation de nouvelles usines de traitement. Une manière efficace de diminuer les dépenses opérationnelles du procédé est de laisser le CAP vieillir dans le contacteur à CAP, et donc de minimiser la dose de CAP. Des études ont mis en évidence le potentiel du PMH opéré avec CAP âgé pour l'enlèvement de l'azote ammoniacal et du COD. Par contre, son potentiel à enlever les micropolluants est inconnu.

La baisse d'efficacité pour l'enlèvement du carbone organique dissous (COD) ainsi que l'augmentation de la capacité d'enlèvement de l'azote ammoniacal avec le vieillissement du CAP démontrent que l'augmentation du temps de rétention du CAP (âge) dans le contacteur peut être associée à l'installation d'une biomasse hétérotrophe et nitrifiante. Il a été suggéré que l'activité bactérienne sur le CAP âgé contribue de façon majeure à l'enlèvement des composés dissous suite à l'épuisement progressif de sa capacité d'adsorption. Cependant, la biomasse bactérienne sur CAP n'a jamais été quantifiée, faute de méthode adéquate. En outre, l'importance de la capacité d'adsorption résiduelle du CAP âgé pour l'enlèvement de composés dissous est inconnue. En fait, les mécanismes responsables de l'enlèvement des composés dissous par le CAP âgé n'ont jamais été différenciés.

Actuellement, la plupart des études publiées sur le PMH opéré avec du CAP âgé ont été réalisées à l'échelle pilote et en eau chaude. Alors que l'adsorption et l'activité biologique sont deux mécanismes sensibles à la température, le potentiel du PMH en eau froide est peu connu. De manière générale, l'opération du PMH avec CAP âgé nécessite des efforts de recherche supplémentaires afin d'être optimisée.

Le principal objectif de cette thèse est de décrire la performance du contacteur à CAP des PMHs pour l'enlèvement de l'azote ammoniacal, du COD, du COD biodégradable (CODB) et des micropolluants. L'emphase est mise sur l'opération du PMH avec de hauts temps de rétention de CAP. Plus spécifiquement, les objectifs de ce projets de recherche sont de (1) développer et comparer des méthodes permettant de quantifier la biomasse développée sur le CAP âgé, (2) développer une méthode permettant de produire un témoin abiotique à partir de CAP colonisé, (3) caractériser les cinétiques d'enlèvement de l'azote ammoniacal, du COD, du CODB et de micropolluants dans le contacteur à CAP du PMH, (4) évaluer l'impact de la température sur la performance du contacteur à CAP d'un PMH, (5) déterminer quelle est l'importance relative de l'adsorption et de l'activité biologique comme mécanismes responsables de l'enlèvement de l'azote ammoniacal, du COD et des micropolluants dans le contacteur à CAP d'un PMH, et (6) différencier l'importance du temps de rétention hydraulique (TRH), de l'âge du CAP et de la concentration de CAP comme paramètres clefs pour l'optimisation de la performance du contacteur à CAP d'un PMH.

La première phase de travail de cette étude a consisté en une série de développements méthodologiques nécessaires à l'étude du CAP âgé. En effet, deux méthodes étaient nécessaires à la réalisation de ce projet de recherche comptant parmi ses objectifs la différenciation les mécanismes responsables de l'enlèvement des composés dissous par le CAP colonisé. Les méthodes développées ont donc pour rôles: i) la quantification de la biomasse hétérotrophe et nitrifiante colonisant le CAP âgé et ii) la production de témoins abiotiques à partir d'échantillons de CAP colonisé. Un nombre important de méthodes a déjà été publié pour quantifier la biomasse bactérienne hétérotrophe et nitrifiante sur le charbon actif en grain (CAG) provenant de filtres biologiques. Aux Chapitre 3 et Chapitre 5, plusieurs de ces méthodes ont été adaptées avec succès au CAP. Le taux de respiration potentiel de glucose (PGR) ainsi que l'activité nitrifiante potentielle (PNA) permettent de quantifier la biomasse active hétérotrophe et nitrifiante. Ces méthodes sont celles favorisées dans ce projet puisque la portion de biomasse active est celle

potentiellement responsable de l'enlèvement des composés dissous dans les contacteurs à CAP. En outre, une méthode alternative à la méthode PGR est proposée, le taux de consommation d'acétate (PAU), afin de réduire les éventuels problèmes logistiques et budgétaires associés à l'utilisation de ^{14}C-glucose. Les résultats des méthodes PAU et PGR étant hautement corrélés (R=0.82), il est donc suggéré au Chapitre 3 que chacune des deux méthodes puissent être utilisées de façon indifférenciée. La mesure de protéines étant aussi hautement corrélées au PGR (R=0.89) et au PAU (R=0.80), c'est la méthode recommandée pour la mesure de biomasse hétérotrophe sur site. La méthode PAU ainsi que l'ensemble des méthodes adaptées du CAG au CAP ont mis en évidence la présence d'une densité de biomasse bactérienne hétérotrophe et nitrifiante sur CAP de 10 et 60 jours comparable à celle mesurée sur du CAG échantillonné en surface de filtres biologiques.

L'irradiation aux rayons gamma ayant été démontrée comme étant une méthode adéquate pour la production de témoins abiotiques dans les sols, elle est la méthode choisie pour produire des témoins abiotiques de CAP colonisé dans ce projet de doctorat (Chapitre 4). Le défi associé à la production de témoins abiotiques consiste en la capacité de la méthode choisie à inhiber efficacement l'activité bactérienne et ce, sans affecter les caractéristiques d'adsorption (capacité et cinétique) de l'échantillon de CAP traité. À des fins d'optimisation de la méthode, six échantillons d'un même CAP colonisé ont été exposés à des doses croissantes de rayonnement gamma. Des cinétiques d'adsorption de bleu de méthylène, modélisées par un pseudo-deuxième ordre (PSO), ont été réalisées sur ces six échantillons. Une dose supérieure à 15 kGy ayant modifié la cinétique d'adsorption, la dose maximale tolérée a été fixée à 15 kGy. En parallèle, des comptages de bactéries hétérotrophes sur gélose (HPC) ont été réalisés pour chacun des échantillons irradiés afin de déterminer la dose minimale de rayons gamma requise pour inhiber la croissance bactérienne hétérotrophe (10 kGy). Sur base des cinétiques d'adsorption du bleu de méthylène et des comptages bactériens, une dose optimale de rayons a donc été recommandée (10-15 kGy). Afin de confirmer l'efficacité de l'irradiation et le bon choix de la dose, des cinétiques d'adsorption du COD réfractaire (CODR) ont été suivies puis modélisées (PSO). Les paramètres de cette cinétique (capacité d'adsorption et cinétique d'adsorption) n'ayant pas été affectés par l'irradiation, ces essais confirment que les caractéristiques d'adsorption du CAP colonisé irradié n'ont pas été altérées. Le développement des méthodes de PGR et PAU ayant rendu possible la quantification de la biomasse bactérienne hétérotrophe active, ces méthodes ont

été utilisées pour confirmer l'efficacité de la dose de rayons optimisée pour l'inhibition de l'activité biologiques hétérotrophe sur les échantillons de CAP colonisé. L'irradiation à la dose optimisée a permis de réduire l'activité hétérotrophe bactérienne (exprimée en PGR) de 83%. La méthode par irradiation aux rayons gamma se révèle donc efficace pour les échantillons de CAP colonisé et a donc été utilisée dans les phases de travail subséquentes. Étant donné la variabilité de la sensibilité des différentes espèces bactériennes au rayonnement gamma, il est recommandé d'optimiser le dosage des rayons gamma pour tout projet prévoyant d'employer cette méthode.

La seconde partie de cette étude s'est concentrée sur l'étude de l'efficacité du PMH pour l'enlèvement de l'azote ammoniacal (Chapitre 5), du COD (Chapitre 6), ainsi que d'un ensemble de micropolluants (Chapitre 7).

Au Chapitre 5, l'enlèvement d'azote ammoniacal au sein du contacteur à charbon du PMH a été simulé en laboratoire. Les cinétiques d'enlèvement ont été suivies en présence de trois concentrations de CAP (environ 1, 5 et 10 g/L), de trois CAP d'âge variable (0-d, 10-d et 60-d), sous deux conditions de températures contrastées (7 et 22°C) et ce, dans deux matrices d'eau décantée différentes (naturelle avec environ 100 µgN-NH_4/L et cette même eau décantée mais dont la concentration en azote ammoniacal a été dopée à environ 1000 µg/L). Étant donné que l'irradiation aux rayons gamma n'a pas été validée pour les bactéries nitrifiantes, la production de nitrites et de nitrates a été employée comme indicateur de la fraction d'azote ammoniacal nitrifiée. Dans les conditions de colonisation étudiées, la colonisation du CAP par les bactéries nitrifiantes ne semble pas avoir été limitée par l'espace disponible (5-10 g/L) et par conséquent, la concentration en CAP ne s'est pas révélée être un paramètre d'opération clef pour l'enlèvement de l'azote ammoniacal dans les conditions testées, c'est-à-dire pour autant que suffisamment de support à la croissance de biomasse nitrifiante est présent. Au contraire, la charge en azote ammoniacal est apparue comme un élément limitant pour la croissance bactérienne (TRH de 67 min). Concernant l'impact de l'âge sur le traitement, le CAP de 60 jours s'est révélé plus efficace à 7°C que le CAP de 10 jours puisqu'il a permis de maintenir un enlèvement de 78% de l'azote ammoniacal alors que le CAP de 10 jours n'a pas permis d'atteindre un enlèvement supérieur à 10% à cette même température. Les travaux de laboratoire à 7°C et à 22°C ainsi que le suivi des concentrations de nitrites et de nitrates ont mis en évidence que l'activité bactérienne restait plus élevée à 22°C sur le CAP de 60 jours que sur celui de 10 jours et qu'il existait aussi une adsorption d'azote ammoniacal significative sur le CAP de 60-d et

pas sur celui de 10-d dans la matrice d'eau décantée. Il est suggéré que l'adsorption de l'azote ammoniacal dans le réacteur à CAP de 60 jours ait lieu à la fois sur le CAP lui-même, mais aussi sur les matières en suspension accumulées dans le réacteur. En cas de pic de pollution dans l'eau brute, l'activité nitrifiante observée était relativement faible. Une limitation par la disponibilité en phosphate est suggérée. Néanmoins, un mélange d'adsorption et de nitrification a tout de même permis de maintenir un enlèvement d'azote ammoniacal de 50% sur CAP de 10 jours et de 60 jours à 22°C, et ce alors que la concentration en contaminant à l'entrée avait été augmentée de 10 fois. Un modèle original basé sur les cinétiques d'enlèvement de l'azote ammoniacal a été développé. Ce modèle prédictif permet de déterminer l'importance relative de l'adsorption et de la nitrification pour l'enlèvement de l'azote ammoniacal dans les contacteurs à CAP colonisé dans les conditions étudiées.

Au Chapitre 6, des simulations en laboratoire ont été effectuées pour tester l'enlèvement du COD, du CODB et du CODR dans le contacteur à CAP d'un PMH. Une approche et des conditions opératoires similaires à celles employées pour le suivi de l'azote ammoniacal ont été appliquées pour le COD, à l'exception des matrices d'eau employées (eau décantée et eau brute). Dans le cas du suivi du carbone organique, la concentration en azote ammoniacal n'a pas été altérée. Par contre, le rapport de concentration entre le CODB et le COD a été modifié par la pré-ozonation de la matrice (0 à 1.5 gO_3/gC). Des contrôles abiotiques pour les CAPs 10 et de 60 jours ont été produits sur base de la méthode optimisée au Chapitre 4. La comparaison des cinétiques obtenues sur les CAPs colonisés et leurs contrôles abiotiques respectifs a permis de démontrer que, dans les conditions testées, la biodégradation ne contribue que de façon marginale à l'enlèvement du COD. L'adsorption du COD, favorisée à 22°C, s'est révélée être le mécanisme principal du traitement. Un modèle original, intégrant la distribution d'âge dans les suspensions des CAP, a été développé afin de décrire la performance des contacteurs à CAP opérés à l'équilibre avec des âges de CAP élevés. Pour un âge moyen de 60 jours, le modèle démontre que c'est la fraction de CAP la plus jeune (25 jours et moins, correspondant à 34% de la masse totale de CAP) qui est responsable de 80% de l'enlèvement de COD. Lors de l'utilisation d'une matrice présentant une concentration initiale en COD plus élevée (eau brute) ou une affinité plus faible pour le CAP (eau décantée pré-ozonée), le modèle démontre que la capacité d'adsorption résiduelle des fractions de CAP plus âgées intervient dans l'enlèvement du COD. L'utilité de la

portion plus âgée de la suspension a donc été démontrée en cas de rapide changement de qualité d'eau à l'entrée du procédé.

Finalement au Chapitre 7, un mélange de micropolluants (atrazine, déethylatrazine (DEA), linuron, microcystine, caféine, carbamazépine, sulfaméthoxazole, diclofénac, progestérone et médroxyprogestérone) a été dosé dans de l'eau décantée pré-ozonée (0.85 gO_3/gC) ou non, à des concentrations représentatives des concentrations mesurées dans les eaux de surface (de 130 ng/L à 33 µg/L en fonction du micropolluant). Les cinétiques d'enlèvement de chacun de ces composés ont été suivies sur une période de 7h à 48h en présence de 1 g/L de CAP neuf, de 10 jours, de 60 jours et de 60 jours irradié aux rayons gamma. Même en présence de matière organique naturelle (COD d'environ 3 mgC/L), les micropolluants dosés dans la matrice ont rapidement été adsorbés par le CAP. Aucune biodégradation n'a été mise en évidence pour les 5 composés potentiellement biodégradables (diclofénac, caféine, microcystine, progestérone, médroxyprogestérone). Un enlèvement de 90% de chacun des composés a été atteint facilement en moins de 5 min à la fois sur CAP neuf et sur CAP colonisé. Par contre, il a été plus difficile d'atteindre un enlèvement de 99%, et ce en particulier pour l'atrazine, le DEA et la caféine. L'âge du CAP a, pour ces trois composés, conduit à un ralentissement des cinétiques d'adsorption. Aucun impact sur la capacité d'adsorption de ces trois composés n'a pu être observé. Globalement, 95% de chacun des composés a été adsorbé en moins de 5 min. La compétition directe avec la matière organique n'a pas influencé l'efficacité du procédé pour ces composés dosés à des concentrations représentatives de celles rencontrées dans l'environnement. Par conséquent, le PMH opéré pour l'enlèvement d'azote ammoniacal et de COD semble efficace pour le contrôle d'évènements transitoires de pollutions en micropolluants. Ainsi, il a été possible en laboratoire de rencontrer les recommandations de l'Organisation Mondiale de la Santé pour l'atrazine (2 µg/L) et la microcystine (1 µg/L). Par contre, les conditions opératoires appliquées pour le CAP de 10 jours et de 60 jours n'ont pas permis de rencontrer les règlementations européennes beaucoup plus strictes (Atrazine et DEA : 0.1 µg/L). Pour atteindre un tel degré de qualité d'eau traitée, le PMH devrait alors être optimisé spécifiquement à cette fin.

Ce projet de recherche permet donc de répondre aux interrogations suivantes : La capacité d'adsorption résiduelle des suspensions de CAP âgées contribue-t-elle de façon significative à la performance du HMP pour l'enlèvement de l'azote ammoniacal, du COD et des micropolluants? Parmi l'âge du CAP, la concentration en CAP et le TRH, y a-t-il un paramètre opératoire clef

pour l'enlèvement de l'azote ammoniacal, du COD et des micropolluants? De manière générale, les travaux réalisés au cours de ce doctorat mettent en évidence le rôle de l'adsorption résiduelle sur l'enlèvement de la contamination dissoute, et ce même lorsque le CAP est âgé de 60 jours. Alors que l'enlèvement d'azote ammoniacal a majoritairement lieu par nitrification en eau décantée, le COD et les micropollutants sont principalement adsorbés sur le CAP colonisé. La capacité d'adsorption résiduelle des suspensions de CAP âgées agit aussi comme tampon lorsque le PMH doit faire face à une augmentation soudaine de la concentration en azote ammoniacal, en COD ou en micropolluants. Le suivi des cinétiques d'enlèvement a permis de démontrer que les trois paramètres d'opérations d'intérêt sont inter-reliés. D'un point de vue économique, un TRH inférieur à 15 min est néanmoins désiré pour limiter les coûts du procédé. Par ailleurs, l'intérêt économique associé à l'augmentation de l'âge du CAP peut-être atténué par le besoin d'augmenter la concentration en CAP si l'adsorption est le mécanisme nécessaire au traitement. De façon générale, il est donc recommandé d'optimiser le PMH à l'échelle pilote car les objectifs de traitement, la qualité de l'eau à traiter et le fait les 3 paramètres d'opération soient inter-reliés complexifient l'optimisation du PMH.

En outre, il est recommandé de poursuivre les efforts de recherche sur les suspensions de CAP âgé. En effet, au cours de ce projet de recherche, il est démontré que les conditions opératoires appliquées au cours du vieillissement du CAP ont un impact majeur sur les conclusions du projet. La faible concentration en CODB dans l'affluent du pilote a notamment été un facteur déterminant sur les conclusions de ce travail. Il est donc recommandé d'approfondir la recherche sur l'enlèvement de COD dans des suspensions de CAP âgées avec cette fois un pilote alimenté par une eau plus riche en CODB. Des études supplémentaires devraient en outre caractériser la capacité ainsi que les cinétiques d'adsorption du CAP colonisé et inclure la description de la biodégradation du CODB dans les modèles. Par ailleurs, les résultats obtenus pour l'enlèvement de micropolluants sont prometteurs, mais des recherches supplémentaires sont néanmoins requises pour confirmer l'efficacité du procédé sous des conditions plus variées.

L'une des priorités lorsque l'optimisation du PMH est visée, est de minimiser le TRH. Dans ce projet, il est recommandé d'appliquer un TRH d'au moins 15 min afin de tirer avantage de l'adsorption et de l'activité biologique potentielle. En effet, lors de l'opération de filtres biologiques, un TRH de 10 à 15 min peut être suffisant pour optimiser l'activité bactérienne. Cependant, les filtres biologiques et les suspensions de CAP sont deux types de réacteurs très

différents. Alors que les filtres biologiques se comportent plus comme des réacteurs piston, la suspension de CAP tend vers un mélange parfait. Il est recommandé que les prochains efforts de recherche se concentrent sur l'optimisation du mélange du contacteur à CAP du procédé.

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AC	Activated Carbon
ATZ	Atrazine
BDOC	Biodegradable Dissolved Organic Carbon
BAC	Biological Activated Carbon
C	Ceramic
CA	Cellulose Acetate
CAF	Caffeine
CAPEX	Capital Expenditure
CBZ	Carbamazepine
CC	Carbon Contactor
CD	Cellulose Derivative
CE	Cellulose Esters
CFU	Colony-Forming Unit
CFV	Crossflow Velocity
DCF	Diclofenac
DBP	Disinfection Byproduct
DEA	Deethylatrazine
DL / LD / MDL	Detection Limit / Limit of Detection / Method Detection Limit
DOC	Dissolved Organic Carbon
DW	Drinking Water
dw	dry weight
DWTP	Drinking Water Treatment Plant
EBCT	Empty Bed Contact Time

EPS	Extracellular Polymeric Substances
GAC	Granular Activated Carbon
HAs	Humic Acids
HAAs	Haloacetic Acids
HPC	Heterotrophic Plate Counts
HMP	Hybrid Membrane Process
HRT	Hydraulic Retention Time
LIN	Linuron
LPMs	Low-Pressure Membranes
MB	Methylene Blue
MBR	Membrane Bioreactor
MC	Microcystin
MEDRO	Medroxyprogesterone
MF	Microfiltration
MIB	2-methylisoborneol
MP	Micropollutant
MW	Molecular Weight
MWCO	Molecular Weight Cut Off
NA	Not Available
ND	Non Detected
NF	Nanofiltration
NOM	Natural Organic Matter
NSERC	Natural Sciences and Engineering Research Council
OPEX	Operational Expenditure

PAC	Powder(ed) Activated Carbon
PAN	Polyacrylonitrile
PAU	Potential Acetate Uptake
PE	Polyethylene
PES	Polyethersulfone
PGR	Potential Glucose Respiration
PROG	Progesterone
PNA	Potential Nitrifying Activity
PO	Polyolefin
Pre-O_3	Pre-ozonated
PSO	Pseudo-Second Order
PVDF	Polyvinylidene Fluoride
RC	Regenerated Cellulose
RDOC	Recalcitrant Dissolved Organic Carbon
RO	Reverse Osmosis
RW	Raw Water
SDS-THM	Simulated Distribution System Trihalomethane
SMX	Sulfamethoxazole
SOCs	Synthetic Organic Compounds
SRT	Solids Retention Time
SS	Separation Step
SW	Settled Water
THM	Trihalomethane
THMFP	Trihalomethanes Formation Potential

TMP	Transmembrane Pressure
TOC	Total Organic Carbon
T&O	Taste and Odors
UF	Ultrafiltration
ww	wet weight

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INTRODUCTION

Background

As early as the seventeenth century with the first microorganism observations under a microscope, it became clear that technologies enabling the treatment of large quantities of water were going to be needed in order to maintain the water supply of growing human settlements. During the second half of the nineteenth century, the elimination of waterborne diseases, in particular cholera and typhoid fever was a major concern. Over that period, slow sand filtration became the first treatment widely recognized to reduce epidemic risks.

In the twentieth century continuous chlorination for bacteriological and virus control became the norm, as reaching microbiologically safe water was crucial for treatment facilities. Optimizing chlorination operating conditions became a growing concern in the 1970s, following evidence of the production of haloforms stemming from the reaction between natural organic matter and chlorine (Rook, 1976). Avoiding disinfection byproducts (DBP) formation therefore became another key issue for Public health, as they were suspected to be carcinogenic. In 1993, the Milwaukee Cryptosporidiosis outbreak drew attention towards the disinfection of pathogens with high levels of resistance to treatment (*Giardia* and *Cryptosporidium spp*). These highly resistant pathogens increased the pressure on drinking water treatment facilities by another notch, forcing them to comply with microbiological and DBPs regulations. In addition, regulation compliance was expected all the way down to the consumer's tap, emphasizing the need to reduce the potential for bacterial regrowth in the produced drinking water.

Nowadays, the drinking water industry is facing yet another challenge as novel analytical techniques have increased the general public's concerns about emerging trace contaminants in drinking water sources as well as in treated drinking water (Coupe et al., 2004; Daneshvar et al., 2012; Huerta-Fontela et al., 2011). Topical drinking water treatment therefore encompasses the following objectives:

i) to disinfect/inactivate the pathogens of concern;

ii) to avoid DBPs formation and minimize the chlorine demand of water (i.e. ammonia, NOM removal);

iii) to achieve drinking water biological stability (i.e. biodegradable NOM removal), and more recently,

iv) to remove the trace organic contaminants.

Since the 1900s, the conventional treatment, consisting in coagulation+flocculation, sedimentation and filtration, is predominant (Logsdon et al., 2006). Due to stricter regulations, this conventional treatment has required improvements. In the 1970s, replacing the filter medium (e.g. anthracite) by granular activated carbon (GAC) improved water quality by removing organics causing taste and odor issues (Logsdon et al., 2006). Adding post-UV disinfection to the process also helped inactivate the preoccupying *Cryptosporidium spp.* (Cotton et al., 2001). Unfortunately, the required regeneration of the filtering media (GAC) can be expensive. In the 1980s, the first GAC filters were converted to biologically active GAC (BAC) filters, and preceded by ozonation. Using the combination of ozone and BAC filters produced biostable drinking water with a reduced chlorine demand and a reduced risk of DBP formation (Prévost et al., 2005). The replacement costs of GAC were greatly reduced. However, ozonation of the natural organic matter increases its biodegradability (De Laat et al., 1991) which can cause regrowth issues in water distribution systems if not treated in the drinking water facilities (Prévost et al., 2005). Furthermore, the efficiency of BAC filters is highly dependent on water temperature (Andersson et al., 2001), which can be an issue in countries with large seasonal variations such as Canada. Finally, adsorption sites being largely exhausted, recalcitrant (i.e. non-biodegradable) contaminants removal is limited (e.g. saxitoxin) (Newcombe, 2002). The need for more efficient and innovative technologies is obvious.

The most significant process development in modern drinking water production is likely membrane filtration. Regulations on water disinfection (i.e. *Cryptosporidium spp.*) and more recently cost reductions on membrane filtration units have favored their installation. Using membranes is now almost systematically considered in existing facilities upgrade studies or on new designs. The number of drinking water facilities using high pressure nanofiltration (NF) membranes increased during the 1990s due to their potential to remove dissolved organics (e.g. pesticides, DBPs precursors), inorganics (e.g. ammonia) and their ability to disinfect water in a single-step (Logsdon et al., 2006). Nevertheless, low-pressure membranes (MF/UF) are now preferred over high-pressure membranes (NF) due to high operational costs and expensive

pretreatment (Hilal et al., 2004). In 2005, 450 MF/UF facilities were listed in 38 countries, 48% of which were located in North America (Adham et al., 2005).

MF/UF membranes are highly efficient to remove particulate material (e.g. microbial contaminants, turbidity) (Jacangelo et al., 1997; Laîné et al., 2000) but ineffective against dissolved contaminants such as NOM, ammonia, MIB, geosmin, toxins, pesticides, pharmaceuticals or hormones (Chorus et al., 1999; Huang et al., 2009; Laîné et al., 2000; Reiss et al., 1999; Suzuki et al., 1998; Yoon et al., 2007). Yet, the usage of MF/UF membranes can be expanded by adding pre- or post-treatment targeting dissolved contaminants. Pre-coagulating the water enables higher NOM removals (Huang et al., 2009). BAC filters were also added before or after the membrane filtration in full-scale drinking water treatment plants (DWTP) (Lakeview DWTP, ON, 363 MLD and Twin Oaks DWTP, San Diego County, 378 MLD). However, in addition to the weaknesses of BAC filters mentioned above, they also present an elevated footprint that can outweigh benefits stemming from the lower footprint of membranes.

In this context, the combination of low-pressure membranes with a powdered activated carbon (PAC) contactor emerges as a well-adapted and yet low-cost solution to treat surface waters. This association between the MF/UF membranes and the PAC is referred to as the Hybrid Membrane Process (HMP). A technology of HMP coupling adsorption on PAC with low pressure membrane filtration was patented by Veolia Water under the name Opaline™. This technology exists under two layouts. In the first configuration, the membranes are submerged in a suspension of PAC (Opaline B®). This configuration has the advantage of presenting a small footprint. In the second configuration, a PAC contactor precedes the usage of pressurized membranes (Opaline S®). In this arrangement, the PAC is not in contact with the membranes, which enables higher operating fluxes thanks to pressurized membranes. The Opaline™ technology (HMP operated at low PAC residence times) is already applied at full-scale in 24 locations with flow capacities ranging from 300 to 160 000 m³/d (*Veolia Eau Solutions & Technologies | Opaline™ - Références*, 2014). Unfortunately, the corresponding environmental and operating costs are high. Furthermore, ammonia adsorption on activated carbon is considered marginal (Bandosz et al., 2009). There is therefore an interest in optimizing less expensive operating alternatives for the HMP.

Operating the HMP with aged PAC (i.e. after establishment of a bacterial biomass at its surface) appears environmentally and economically viable given it can easily be done with high PAC

residence times (Lebeau et al., 1998). Colonized PAC's potential for the removal of dissolved organic carbon (DOC), ammonia, dissolved manganese, and DBPs precursors has been established (Lebeau et al., 1998; Suzuki et al., 1998; Treguer et al., 2008; Watanabe et al., 2000; Williams et al., 2007). Recalcitrant contaminants, including pesticides, require however to be adsorbed on new PAC. The potential of the HMP operated with aged PAC to remove these recalcitrant contaminants is unknown. Nonetheless, by relying on the permanent possibility to increase the dosage of PAC, this new generation of processes brings an added benefit: flexibility. Indeed, seasonal variations in dissolved contaminant concentrations or punctual deterioration of the source water quality can then be directly offset by shifting from the economical aged PAC-based process to an adsorption-only process by decreasing the PAC residence time.

As suggested by the rising number of publications on the topic, the HMP appears as a promising new process. The existing literature mostly covers pilot-scale studies that demonstrated the great potential of the HMP to reach high drinking water quality using PAC as an adsorbent. Yet, many challenges remain to describe the performance of the PAC contactor of the HMP. The potential of using the HMP with aged PAC to reach drinking water biostability (i.e. ammonia and biodegradable DOC removal) under cold water conditions remains to be proven. Its efficiency in removing emerging contaminants (algal toxins, pharmaceuticals, hormones, etc.) has also yet to be substantiated.

Structure of dissertation

This manuscript is subdivided in 8 Chapters. First of all, the current state of knowledge on the hybrid membrane process is presented in an in-depth review published in *Journal of Membrane Science* (Chapter 1), followed by the goals of the proposed project and the methodology developed (Chapter 2). In Chapter 3 through Chapter 7, the reader will find the research that constitutes the core of this manuscript. These chapters are papers that were either published or submitted to peer-reviewed journals. Chapter 3 and Chapter 4 cover the methodological aspects of the proposed project. Chapter 3 presents methods to quantify the bacterial biomass at the surface of colonized PAC (published in *Journal of Water Supply: Research and Technology – AQUA*). Chapter 4 provides a method to produce an abiotic control from colonized PAC (published in *Environmental Technology*). Chapter 5 to Chapter 7 are devoted to i) confirm the potential of the HMP operated at high PAC retention times for dissolved contaminants removal,

ii) determine the relative contribution of the mechanisms responsible for the treatment when using colonized PAC and iii) determine the key operating parameters for the operation of the PAC contactor in an HMP. Chapter 5 focuses on ammonia removal (currently under review for *Water Research*), Chapter 6 on dissolved organic carbon removal (submitted to *Water Research*) and finally Chapter 7 is devoted to trace organic contaminants removal (submitted to *Journal of Hazardous Materials*). A general discussion is provided in Chapter 8, with conclusions and recommendations completing this manuscript.

CHAPTER 1 ARTICLE 1 - HYBRID MEMBRANE PROCESSES USING ACTIVATED CARBON TREATMENT FOR DRINKING WATER: A REVIEW

This chapter includes a literature review that provides the current state of scientific knowledge regarding the use of HMPs for the production of drinking water. In particular, performances in terms of water quality and membrane fouling are reviewed. This chapter was published in the *Journal of Membrane Science*. Supplementary information of this article is provided in APPENDIX 1.

HYBRID MEMBRANE PROCESSES USING ACTIVATED CARBON TREATMENT FOR DRINKING WATER: A REVIEW

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ABSTRACT

More stringent regulations on drinking water quality as well as an increased focus on emerging contaminants have favored the development of alternative technologies to the conventional process (clarification + filtration + chlorination). Over the last decade, low pressure membrane filtration coupled with activated carbon has been emerging as a promising solution, often termed as the Hybrid Membrane Process. Combining activated carbon with membranes presents numerous challenges including membrane abrasion, membrane fouling, optimization of operating conditions, prediction of process performances and selection of the process configuration. This paper presents a review of the current knowledge concerning the use of the Hybrid Membrane Process, applied either under a biological or an adsorption mode, in view to produce drinking water. The paper reviews the alternative process layouts and discusses their expected performances with respect to water quality and membrane fouling.

KEYWORDS

Activated carbon - Hybrid Membrane Process – Fouling – Adsorption - Biological treatment

1.1 Introduction

Over the last decade, the tightening of water quality regulations and the increased attention given to trace contaminants has been favoring the emergence of alternative treatment technologies in order to upgrade or improve the conventional treatment process (clarification + filtration + chlorination). The later offers a limited ability with regards to natural organic matter (NOM) (Bouwer et al., 1988), synthetic organic compounds (SOCs) and disinfection byproducts (DBPs) removals (Crozes et al., 1993; Fane, 1996; Jacangelo et al., 1995; Kim et al., 2005; Tomaszewska et al., 2002). Achieving high removal of protozoan parasites is also a challenge while using conventional treatment (Betancourt et al., 2004).

Many modifications have been proposed to improve the performance of conventional treatment processes. One alternative consists of converting sand-anthracite filters into biological granular activated carbon (GAC) filters preceded by ozonation. Ozonation can effectively reduce taste and odors (T&O), improve disinfection, reduce the formation potential of trihalomethanes (THMFP)

and haloacetic acids (HAAs), as well as oxidize many trace organic contaminants (Wobma et al., 2000) and increase dissolved organic carbon (DOC) biodegradability (De Laat et al., 1991). The biological GAC filters can effectively remove some algae toxins (Newcombe, 2002), ammonia (Bouwer et al., 1988), biodegradable organic carbon (Bouwer et al., 1988; Janssens et al., 1985) and many trace organic contaminants including T&O compounds such as 2-methylisoborneol (MIB) and geosmin (Elhadi et al., 2006; Westerhoff, Summers, et al., 2005). However, the ability of such systems to effectively remove certain pathogens, such as *Cryptosporidium*, especially in cold climates, is limited. The effective removal of *Cryptosporidium* could be achieved by adding UV disinfection following ozonation and biological GAC filtration. However, this would significantly add to the capital and operating costs of the system.

Microfiltration (MF) and ultrafiltration (UF) are increasingly being considered as alternatives to granular media filtration (Huang et al., 2009; Jacangelo et al., 1995; Laîné et al., 2000; Suzuki et al., 1998). MF and UF membranes, hereafter simply referred to as low pressure membranes (LPMs), can effectively remove particulate contaminants, including protozoan parasites such as *Cryptosporidium*. However, membranes cannot effectively remove dissolved NOM, SOCs and compounds responsible for T&O and color (Huang et al., 2009; Laîné et al., 1990; Laîné et al., 2000; Lebeau et al., 1998; Suzuki et al., 1998). Consequently, in order to improve treatment performance, LPMs have been coupled with other processes, mainly coagulation, ozonation or adsorption. Among these alternatives, combining activated carbon with LPMs has received increasing consideration over the last two decades (Adham et al., 1991). In the mid-nineties, hybrid membrane processes were described as processes where "*one or more membrane process is coupled with another unit process such as adsorption, ion exchange, coagulation, bioconversion, catalysis, etc.*" (Fane, 1996). However, the recent scientific literature mostly focuses on the hybrid membrane process (HMP) that combines powdered activated carbon (PAC) and LPMs under a variety of configurations (Jia et al., 2009; Markarian et al., 2010; Mozia et al., 2004; Oh et al., 2007; Saravia et al., 2006; Song et al., 2009; Suzuki et al., 1998; Treguer et al., 2008). In the discussion which follows, HMP is defined as a process that combines low-pressure driven membrane filtration with a carbon contactor (CC). The carbon contactor (CC) is a reactor where the influent water is put in contact with activated carbon (either a GAC filter or a PAC suspension).

The HMP is being increasingly used to improve the ability of membrane systems to remove soluble contaminants. In addition, the use of activated carbon before filtration can reduce membrane fouling (Hallé et al., 2009). This review aims to provide the current state of scientific knowledge regarding the use of HMP for the production of drinking water. The different HMP configurations are first reviewed. The performance of the different configurations in terms of water quality and membrane fouling are then discussed. Finally, a broader discussion will present a critical analysis of further research needs.

1.2 Hybrid Membrane Process

1.2.1 Alternative layouts

The different configurations of HMP can be loosely classified into three categories: i) HMP with activated carbon treatment prior to LPMs filtration (pre-treatment configuration, see Figure 1-1); ii) HMP with an integrated activated carbon treatment and LPMs filtration (integrated treatment configuration, see Figure 1-2) and iii) HMP with activated carbon treatment after LPMs filtration (post-treatment configuration, see Figure 1-3). For each category, dissolved contaminants are predominantly removed by the activated carbon either by adsorption (adsorption mode) or biodegradation (biological mode). A detailed review of the different types of HMP for drinking water treatment is presented in the following sections. Advantages and disadvantages of the three existing configurations are summarized in Table 1-1.

1.2.1.1 HMP with an activated carbon pre-treatment

When the CC is placed before the LPMs, raw (or pretreated) water is first introduced in the CC and then filtered through the LPMs filtration unit. The CC can either be an adsorptive GAC filter or a biological GAC filter (e.g. : Lakeview, Ontario, 363 MLD), a fluidized GAC suspension (e.g. the Carboplus® process) or a PAC contactor where PAC is maintained in suspension, dosed and purged to obtain the desired age and concentration. The PAC contactor effluent is then sent to the LPMs.

The LPMs can be pressurized or immersed and operated in both cases either under an outside-in or an inside-out mode. Pressurized systems can be operated with or without crossflow. The crossflow from the membrane is often recirculated to the PAC contactor (see Figure 1-1– option A). This strategy enables the system to recycle the PAC sludge and increase the PAC effective

contact time, thus minimizing PAC dosage. Alternatively, a separation step can also be installed at the effluent of the CC in order to achieve the same goal as the recirculation (increase contact time) (see Figure 1-1– option B). The configuration consisting of a PAC contactor, pressurized membranes and a recirculation loop (option A) is already operated at industrial scale in France and is referred to as the CRISTAL® process (Ex: Vigneux, France, 55 MLD) (Baudin et al., 1997; Campos et al., 1998) while option B is commercialized as the Opaline™ S process (Ex: L'Haÿ-les-Roses, 150 MLD).

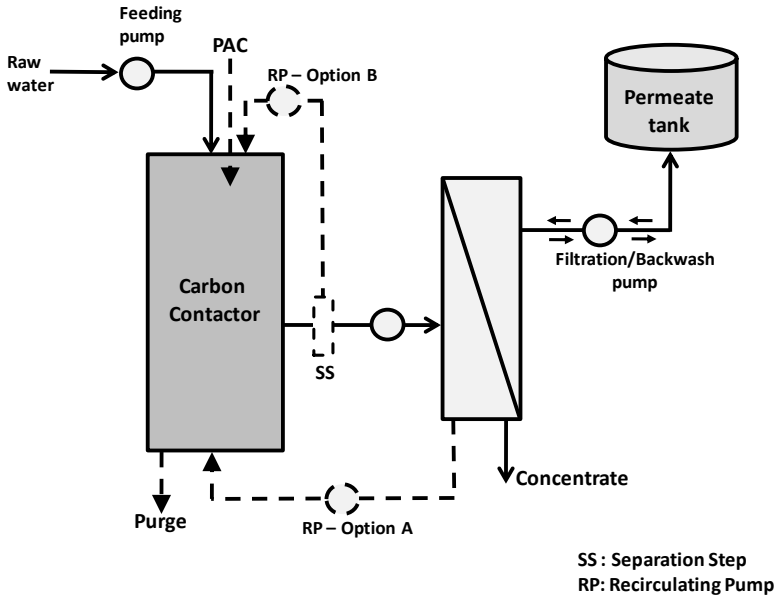


Figure 1-1 : Schematic representation of the HMP with activated carbon pre-treatment. When PAC is used, the concentrate can be either recirculated in the CC (Option A) or separated using a separation process before being recirculated (Option B)

1.2.1.2 HMP with an integrated activated carbon treatment

In the integrated configuration, activated carbon, as PAC, is added directly to the influent raw (or pretreated) water of a submerged LPMs system. Aeration is provided to avoid PAC sedimentation and reduce fouling. The membrane enables relatively high concentrations of PAC to be maintained in the system. Excess PAC is either continuously or periodically purged from the system. Since the age of the PAC can be easily controlled by purging, the system can be operated either in an adsorption or a biological mode, depending on the age of the PAC. To our knowledge, this configuration has never been applied at full scale.

Recently, the use of a membrane bioreactor (or MBR), a biological process typically used in wastewater treatment, coupled to PAC was investigated to treat highly polluted surface waters for drinking water production. With this strategy, the MBR is combined with PAC adsorption within the mixed liquor. This new process aims to take advantage of the substantial adsorption capacity of PAC with the ability of MBR to effectively remove ammonium as well as low-molecular and biodegradable organic substances (Sagbo et al., 2008; Tian et al., 2009; Tian et al., 2010; Tian et al., 2008; Tsai, Ravindran, et al., 2004). This approach was not considered in the current review.

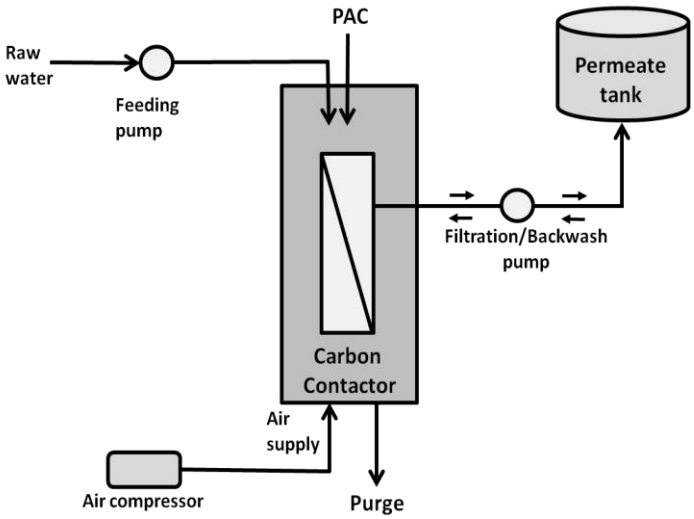


Figure 1-2 : Schematic representation of the HMP with integrated activated carbon treatment

1.2.1.3 HMP with an activated carbon post-treatment

When LPMs are placed ahead of the CC, the later is typically operated as a GAC filter. Fluidized GAC or PAC reactors are problematic as activated carbon fines can be exported from the process along with the treated water. Therefore, an additional physical separation process is needed under such configuration. This has not been common in full-scale applications. On the other hand, the use of post-GAC filters is fairly common. For example, the 400 MLD Twin Oaks water treatment plant (CA, USA) uses such treatment scheme with the difference that ozonation is used prior to the GAC filters (San Diego County Water Authority, 2008).

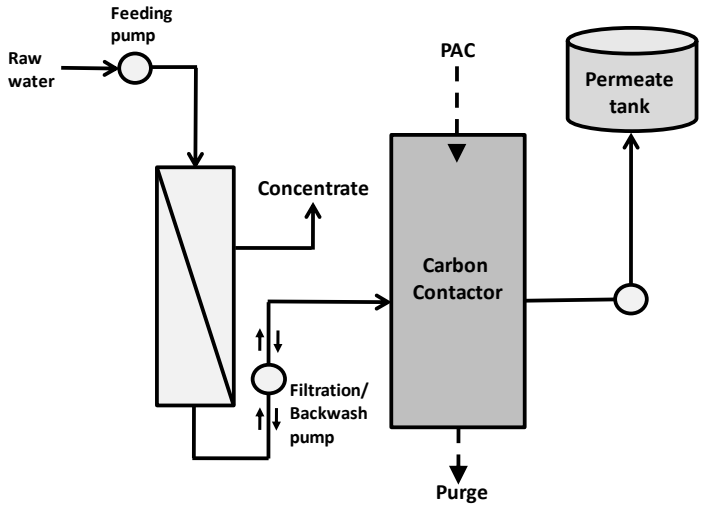


Figure 1-3 : Schematic representation of the HMP with activated carbon post-treatment

Table 1-1 : Advantages and disadvantages for the 3 existing configurations of the HMP (HMP with activated carbon pre-, integrated or post-treatment).

Pre-treatment		**Integrated**		**Post-treatment**	
Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages
Possibility to use PAC and GAC		Possibility to use PAC			Carbon contactor must be a GAC contactor, impossibility to use PAC suspensions Risk of exporting carbon fines
Possibility to control the AC age when using PAC suspension		Possibility to control the AC age when using PAC suspension			No possibility to control the AC age
Possibility to use pressurized or immersed membranes		Possibility to use vacuum membranes in existing basins	Importance of maintaining membrane integrity	In case of membrane integrity loss, GAC filter may act as an additional barrier	
PAC not in contact with membrane: higher flux and lower fouling expected	Additionnal separation step is needed if high PAC concentration is used	Membranes insures simultaneous treatment and PAC separation	Lower flux when membranes are in contact with PAC suspension		Higher membrane fouling
	More footprint required due to the use of two treatment steps	Compact process	Fouling Aeration required		More footprint required due to the use of two treatment steps
Existing full scale applications			No full scale application listed	Combination of two proven technologies	

1.2.2 Alternative operational configurations

Activated carbon can be used for its high adsorption capacities of organic matter, cyanotoxins, T&O and color (Hargesheimer et al., 1996; Najm et al., 1990; Newcombe et al., 2004), as well as for its ability to support high heterotrophic and nitrifying biomass (Gai et al., 2008; Kim et al., 2005; Servais et al., 1991; Treguer, 2007; Xiaojian et al., 1991). The dominance of adsorption over biological activity is roughly controlled by the residence time of the activated carbon within the CC (i.e. the age of the activated carbon). For GAC filters operated under adsorption mode, the number of bed volume treated (m^3 of water per m^3 of filter media) is commonly employed for this purpose (Montgomery Watson Harza (MWH), 2005). For biological GAC filters, the time required for colonization will depend on the type of microorganisms and carbon, the temperature, the pH and the available nutrients, and thus may well vary from only a few days to several months (Prévost et al., 2005; Servais et al., 1994).

Replacing media in GAC filters is a cumbersome and expensive activity. Consequently, many systems use biological GAC filters rather than adsorptive GAC filters as a strategy where the media is not replaced and therefore operated essentially under biological mode. Recently, researchers have also investigated the use of PAC under biological mode (Markarian et al., 2010; Treguer, 2007), which could lead to the removal of the biodegradable organic substances and would reduce the costs related to PAC renewal. The interest of this approach lies in the possibility to better control the age of the PAC within the process and, consequently, the system performance. In addition, adding/removing PAC within a CC is a straightforward process compared to GAC media replacement.

Within the HMP, in the PAC reactor under steady-state, the AC is being accumulated so that the Hydraulic Retention Time (*HRT*, in days), which corresponds to the average length of time that the influent remains in the CC, is different from the age of the PAC (θ_{PAC}, in days), which corresponds to the average time spent by the PAC in the reactor. PAC age is defined as the ratio between the mass of carbon in the CC (M_{PAC}, in g) and the mass of carbon purged daily from the reactor. This ratio is equivalent to the ratio between the reactor volume (V_R, in L) and the wasted flow (Q_w, in L/d), assuming that the PAC concentration within the reactor (C_{PAC}, in g/L) is identical to that in the wasted flow (see Eq. 1-1). HRT ranging from 10 to 120 minutes are the most commonly applied in the HMP (Adham et al., 1991; Campinas et al., 2010b; Kim et al.,

2008; Lebeau et al., 1998; Markarian et al., 2010; Oh et al., 2007; Saravia et al., 2008; Suzuki et al., 1998; Treguer et al., 2008; Treguer et al., 2010; Wang et al., 2004; Watanabe et al., 2000), although HRT as high as 300 minutes have been tested (Khan et al., 2009; Pirbazari, Badriyha, Kim, et al., 1992). PAC age as high as 250 days has been considered (Markarian et al., 2010; Seo et al., 2002) although θ_{PAC} between 0 (new PAC) to 60 days is more common (Adham et al., 1991; Campinas et al., 2010b; Campos et al., 1998; Khan et al., 2009; Kim et al., 2007; Kim et al., 2008; Kim et al., 2009; Lebeau et al., 1998; Lee et al., 2009; Markarian et al., 2010; Mozia et al., 2004; Mozia et al., 2005, 2006; Oh et al., 2007; Pirbazari, Badriyha, Kim, et al., 1992; Saravia et al., 2008; Seo et al., 2004; Song et al., 2009; Suzuki et al., 1998; Tomaszewska et al., 2002; Treguer et al., 2008; Treguer et al., 2010; Watanabe et al., 2000; Williams et al., 2007; Xia et al., 2007; Zhao et al., 2005). Values of C_{PAC} ranging from 1 to 40 g/L have been reported in the literature (Khan et al., 2009; Kim et al., 2007; Kim et al., 2009; Lebeau et al., 1998; Lee et al., 2009; Markarian et al., 2010; Oh et al., 2007; Pirbazari, Badriyha, Kim, et al., 1992; Saravia et al., 2008; Seo et al., 2002; Seo et al., 2004; Suzuki et al., 1998; Treguer et al., 2008; Treguer et al., 2010; Williams et al., 2007; Zhao et al., 2005). The impacts of operational conditions on fouling and performance will be discussed in the sections that follow.

$$\theta_{PAC} = \frac{M_{PAC}}{C_{PAC} \times Q_W} = \frac{C_{PAC} \times V_R}{C_{PAC} \times Q_W} = \frac{V_R}{Q_W} \qquad \text{Eq. 1-1}$$

PAC replenishment within the CC can be intermittent or continuous. For the purpose of comparing carbon usage, an equivalent PAC dose (D, in mg/L), defined as the quantity of PAC renewed to treat a given daily volume of water (Q_D, in L/d), and can be estimated using Eq. 1-2. D enables to directly compare the carbon usage of the HMP with the one of a conventional process.

$$D = \frac{M_{PAC}}{\theta_{PAC} \times Q_D} \times 10^{-3} \qquad \text{Eq. 1-2}$$

Equivalent PAC doses generally found in the literature range between 5 and 10 mg PAC/L (Campinas et al., 2010b; Campos et al., 1998; Lebeau et al., 1998; Markarian et al., 2010; Saravia et al., 2008; Song et al., 2009; Treguer et al., 2008; Williams et al., 2007). However, higher

dosages have also been investigated (e.g. 100-200 mg PAC/L) when using PAC as an adsorbent (Jacangelo et al., 1995; Mozia et al., 2004; Mozia et al., 2005, 2006; Tomaszewska et al., 2002). These high values are likely impractical for full-scale steady-state application considering the price of PAC.

1.3 Performances of the HMP

The main trends regarding the performances of the HMP are presented in sections 1.4.1 and 1.4.2. For more detailed information, refer to Table A-1. 1 to Table A-1.8 of the supplementary data.

1.3.1 Overview

1.3.1.1 Disinfection and particulate matter

Membrane filtration (micro- and ultrafiltration) ensures an effective removal of particulate matter, turbidity and some pathogenic microorganisms (protozoa such as *Giardia* and *Cryptosporidium*, pathogenic bacteria) as well as Mn, Fe and Al precipitates (Lebeau et al., 1998; Pianta et al., 1998; Seo et al., 1996). The performance of the HMP for disinfection has not received much attention. Membrane filtration is considered as a disinfection process in water treatment, disinfection resulting mostly due to rejection of pathogens through size exclusion (Madaeni, 1999). Hence, it may be granted log credits for protozoan parasites. However, one could expect some additional removal inside the CC due to flocculation, adsorption and/or grazing.

On the other hand, it is also arguable that the CC concentrates particulate material, especially when the PAC age is high. Under such circumstances, concerns were raised with respect to the potential accumulation of pathogenic organisms in the CC and their release in potable water supplies (Morin et al., 1997) following a breach of integrity of the membranes. Indeed, studies demonstrated that bacterial pathogens may eventually grow on AC surface (Camper et al., 1985b). However, competition for space and nutrients limits the extent of the colonization by pathogens on the AC colonized by an autochthonous microbial community (Camper et al., 1985b). In addition, studies demonstrated that the release of carbon fines does not enhance the number of bacteria in the biofilm of distribution systems and does not provide any protection

against secondary disinfection (Morin et al., 1997). Finally, appropriate ozonation is believed to prevent significant AC colonization by pathogens (Morin et al., 1996). As these studies were realized on GAC filters, it would be of interest to evaluate the fate of pathogens in contact with PAC suspensions. Under the worst-case scenario (i.e. integrated configuration), accumulated pathogens may escape the process if there is a membrane breach. However, because of the high PAC concentration, indirect integrity testing using particles counts or turbidity meters could potentially be used to detect breaches (Guo et al., 2010).

1.3.1.2 Dissolved contaminants

Several studies noted a shift in the process performance as PAC aged, such as i) a decrease in DOC removal (see Figure 1-4, (Kim et al., 2009; Seo et al., 2004)) and ii) the enhancement of nitrification (Barbeau et al., 2010; Kim et al., 2009; Markarian et al., 2010; Seo et al., 2004; Suzuki et al., 1998). However, adsorption efficiency decreases as PAC ages due to sites loading and biofilm development (Simpson, 2008). The period required to shift from a dominant adsorption mode to a dominant biological mode depends on various factors such as temperature, nutrient and substrate load, type of biomass, biomass concentration, type of activated carbon, etc. Results gathered from the literature suggest that PAC older than 20-30 days will be mostly in the biological mode (Barbeau et al., 2010; Kim et al., 2009; Markarian et al., 2010; Seo et al., 2004; Suzuki et al., 1998). Optimization of θ_{PAC} is however still required. It should be noted that there is still a residual adsorption capacity even when the biological mode is predominant and that biodegradation can begin sooner than the 20 to 30 days limit.

Most research has been conducted on the pre- and integrated activated carbon treatment configurations (Figure 1-1 and Figure 1-2). The performance of these two configurations will first be reviewed under adsorption and biological modes. The performances of the activated carbon post-treatment configuration (Figure 1-3) will then be discussed.

1.3.2 Performances of the HMP with pre- or integrated activated carbon treatment

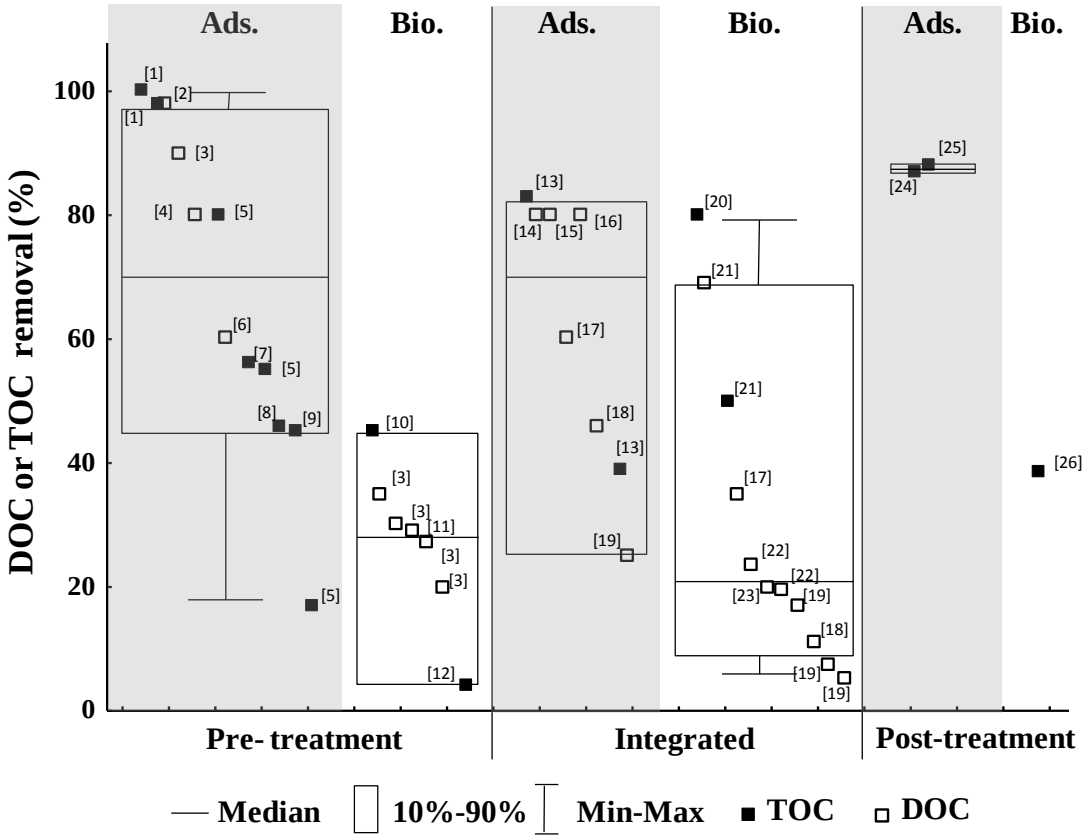
1.3.2.1 Impact of the effluent water quality

When operated in an adsorption mode, both configurations demonstrated high DOC removals (median of 70%, see Figure 1-4) and even higher UV_{254} removals (median of 90% (Adham et al., 1991; Kim et al., 2007; Kim et al., 2008; Kim et al., 2009; Lee et al., 2009; Mozia et al., 2006;

Oh et al., 2007; Seo et al., 2004; Song et al., 2009; Wang et al., 2004; Xia et al., 2007)). Efficiencies increase as PAC dosage (D) (0-200 mg PAC/L) or concentration (C_{PAC}) (4-40 g PAC/L) is increased (Jacangelo et al., 1995; Kim et al., 2007). High UV_{254} removals highlight the efficiency of the process to remove aromatic compounds; an observation that was further confirmed by the 95% DOC removal achieved on a synthetic solution of humic acids and phenols (Mozia et al., 2005, 2006; Tomaszewska et al., 2002). DBPs precursors were also efficiently removed although achieving high removals (THMFP>81%, SDS-THM (Simulated Distribution System THMs): 30-85%) required PAC concentrations within the CC (e.g. 40 g/L) higher than those commonly used in water treatment (Jacangelo et al., 1995; Oh et al., 2007). Finally, the HMP offers high potential for micropollutants removal under the adsorption mode. Removals higher than 90% were documented for selected hormones and pharmaceuticals (Saravia et al., 2008; Song et al., 2009) while atrazine and microcystin removals higher than 50% were achieved (Campinas et al., 2010b; Campos et al., 1998). The efficiency depended on the equivalent PAC dosage ranging from 5 to 10 mg PAC/L. It must be noted that micropollutants were spiked at greater concentrations than those expected to be present in raw water. Also a strong competition was observed between NOM and microcystin, leading to the need for a higher PAC dose (i.e. 10 mg PAC/L) to overcome the NOM presence (Campinas et al., 2010b). In summary, applying the HMP with PAC age under 7 days was proven to be effective to remove DOC, UV_{254} and DBPs precursors as well as various micropollutants. In order to reach sufficient removals, a PAC dose of at least 10 mg/L was needed. Required PAC concentrations within the CC could be as high as 40 g/L (Kim et al., 2007), depending on raw water quality, process configuration and PAC mode of application (continuous versus discontinuous). See Table A-1. 1 and Table A-1. 2 of the supplementary data for more detailed information.

While most research has been conducted with hybrid membrane systems operated with adsorption (i.e. θ_{PAC}<7 days) and mainly focused on NOM and micropollutants removal, research conducted with systems operated with biodegradation has mainly targeted the removal of organic matter and ammonia. As presented in Figure 1-4, the HMP with pre- or integrated activated carbon treatment operated under biological mode maintained DOC removal of 20% (Seo et al., 2004; Treguer et al., 2010) or even exhibited a potential for higher efficiency, obtaining DOC removals above 20% (Lebeau et al., 1998; Seo et al., 2004; Treguer et al., 2008; Williams et al., 2007) in the presence of PAC concentrations varying from 5 to 20 g/L and a PAC dosage ranging

from 5 to 10 mg/L. With PAC age greater than 30 days (i.e. dominance of biological mode), UV_{254} removals (median of 45% (Kim et al., 2009; Seo et al., 2004; Suzuki et al., 1998; Tsujimoto et al., 1998; Watanabe et al., 2000)) were greater than DOC removal (median of 25%, see Figure 1-4). The differences observed between DOC removal efficiencies can be related to the biodegradable DOC (BDOC) content of organic matter while UV_{254} removals depend on its aromaticity. In the biological mode, DOC removal increases when the BDOC/DOC ratio is increased by the conversion of large molecules into smaller ones by pre-ozonation (Treguer et al., 2010). With HMP operated under the biological mode, almost complete nitrification (>90 %) was observed at temperatures from 8.5°C to 25 °C (Lebeau et al., 1998; Seo et al., 2002; Seo et al., 2004; Suzuki et al., 1998; Watanabe et al., 2000); although nitrification performances declined at lower water temperatures (5 to 10°C) (Markarian et al., 2010; Suzuki et al., 1998), ammonia removal was enhanced by increasing PAC concentration from 5 to 25 g PAC/L (Markarian et al., 2010). In river water, ammonia removals of 60-70% were achieved in 10-15 minutes of contact time with PAC of approximately 30 days at 5°C (Suzuki et al., 1998). The complete nitrification that some researchers observed at temperatures as low as 2°C were reached with high ammonia concentrations in the influent (e.g. 5 mg/L) (Seo et al., 2002), which enhanced drastically nitrification kinetics. Finally, it should be noted that the 60 to 70% of ammonia removal that has been observed even at low temperatures contrasts with the reported limited efficiency of nitrification in BAC filters at 1^{o}C (Andersson et al., 2001). DBPs as well as their precursors were efficiently removed by the biological process (HAAs: 92%, THMs: 86% and THMFP: 65 to 85 % depending on the halogen in the THMs) (Khan et al., 2009; Seo et al., 2004). Good T&O removal (ranging from 45 to 80%) was obtained but this efficiency decreased with increasing PAC age (i.e. 10 days versus 40 days) (Treguer et al., 2008). To our knowledge, removal of micropollutants has been poorly studied in the biological mode. Lebeau et al. (1998) obtained high efficiency for atrazine removal (> 90%) using colonized PAC (60 days). As atrazine is difficult to biodegrade, results of Lebeau et al. (1998) confirms that a residual capacity of adsorption for micropollutants is still present in systems operated in biological mode (θ_{PAC} = 60 d). In summary, the performance of the biological mode is somewhat similar or higher than that for the biological GAC filters due to the presence of residual adsorption. See Table A-1. 4 and Table A-1.7 of the supplementary data for more detailed information.



[1] Mozia et al. (2006); [2] Mozia et al. (2005); [3] Williams et al. (2007); [4] Kim et al. (2008); [5] Jacangelo et al. (1995); [6] Pirbazari et al. (1992); [7] Mozia et al. (2004); [8] Xia et al. (2007); [9] Adham et al. (1991); [10] Watanabe et al. (2000); [11] Tsujimoto et al. (1998); [12] Suzuki et al. (1998); [12] Suzuki et al. (1998); [13] Kim et al. (2007); [14] Oh et al. (2007); [15] Zhao et al. (2005); [16] Saravia et al. (2008); [17] Seo et al. (2004); [18] Kim et al. (2009); [19] Markarian et al. (2010); [20] Khan et al. (2009); [21] Lebeau et al. (1998); [22] Treguer et al. (2010); [23] Treguer et al. (2008); [24] Sartor et al. (2008); [25] Schlichter et al. (2004); [26] Niquette et al. (2007)

Figure 1-4 : Published performances of the HMP for DOC (▫) and TOC (▪) removal in % for the 3 existing configurations (HMP with activated carbon pre-, integrated or post-treatment) either under the adsorption (Ads.) or biological (Bio.) mode.

GAC filters have also been used prior to membrane filtration as activated carbon pre-treatment. However, limited information is available in literature on the performance of systems with this configuration. Wang et al. (2004) considered a GAC filter before MF membranes at pilot scale to effectively meet drinking water regulations. The results suggested that GAC was able to adsorb the hydrophobic compounds while microorganisms growing on the GAC surface probably removed the hydrophilic biodegradable matter. The membrane eliminated the bacteria released in

the GAC effluent. The use of biofiltration prior to membrane filtration has mostly been reported for use before reverse osmosis (RO) in wastewater treatment intended for indirect potable water reuse (Gur-Reznik et al., 2008). However, Hallé et al. (2009) studied the effect of biofiltration (with anthracite/sand biofilters) as a pretreatment for ultrafiltration while Tsujimoto et al. (1998) studied the effects of a biological GAC filter pre-treatment. Both studies demonstrated that biofilters helped to improve the permeate water quality and reduced membrane fouling. Hallé et al. (2009) concluded that this type of hybrid process was better suited for small to mid-size systems that do not operate at low temperatures.

1.3.2.2 Impact of the operating conditions

The characteristics of the feed water is of importance since it influences the adsorption capacity of the activated carbon, the microbial development at the PAC surface and the biodegradation kinetics. The pH should remain greater than 6 to maintain stable ammonia oxidation (Seo et al., 2004). While temperature has a major effect on the performances of the process when applied in a biological mode (HMP seems to adapt at low temperature but performances tend to decrease) (Lebeau et al., 1998; Seo et al., 2002; Seo et al., 2004; Suzuki et al., 1998), water composition strongly influences the adsorption of organic matter onto activated carbon. Indeed, competition phenomena between strongly and weekly adsorbable compounds influence the removal performances of PAC (Lebeau et al., 1999). Moreover, salt precipitation (carbonates) at PAC surface may clog the adsorption sites and tend to increase particle settling (Lebeau et al., 1999). Metallic ions also influence adsorption and ion exchange at PAC surface (Zhao et al., 2005).

Pre-ozonation seems to offer the potential to enhance the performances of the hybrid process in the biological mode. Indeed, ozonation increases the BDOC content of the raw water, enabling higher DOC removal, and can reduce the formation potential of THMs and HAAs (Treguer et al., 2008; Treguer et al., 2010). However, pre-ozonation is also responsible for negative effect on the global efficiency of the hybrid process. Indeed, pre-ozonation can also be responsible for the reduction of the adsorption efficiency (Treguer et al., 2010). Therefore, when considering the adsorption mode, a compromise has to be found between the conversion of humic compounds into smaller molecules that diffuse better in PAC pores (Treguer et al., 2010) and oxidation of humic compounds which may lead to a more hydrophilic and less adsorbable NOM fraction (De Laat et al., 1991).

Adsorption is highly enhanced with reduced PAC size (Najm et al., 1990). While PAC size is of major importance for adsorption, it does not appear to be of significant importance for biodegradation (Markarian et al., 2010). Treguer (2007) highlighted the significance of PAC age and PAC concentration on the efficiency of the process used either in an adsorption or a biological mode. Higher PAC concentration leads to higher permeate quality (Kim et al., 2007; Markarian et al., 2010; Treguer, 2007), although this relationship is not linear. PAC ages from 0 to more than 200 days have been investigated. The optimal value depends significantly on the nature of the compounds to remove (Markarian et al., 2010) and the performance targets. In the 10 days to 40 days range, T&O removals were slightly lower with 40 days PAC than with 10 days PAC and DOC removals remained fairly independent of PAC age (Treguer et al., 2008). However, a higher PAC age could reduce the process efficiency due to the excessive accumulation of suspended/adsorbed contaminants inside the reactor (Treguer et al., 2008). In fact, a very high PAC age (200 days) was demonstrated to reduce treatment performances in terms of ammonia, DOC, BDOC and THMFP removals (Barbeau et al., 2011).

Finally, there is little information concerning the hydraulic retention time, Markarian et al. (2010) demonstrated no improvement in the treatment performance with retention time greater than 30 min.

1.3.3 Performances of the HMP with activated carbon post-treatment

1.3.3.1 Impact of the effluent water quality

Limited published literature exists on the use of the post-treatment layout for drinking water treatment (Andersson et al., 2001; Gur-Reznik et al., 2008; Tsujimoto et al., 1998) (information summarized in the Table A-1.8 of the supplementary data). This is probably explained by the fact that this layout combines two processes, LPMs and GAC filters (biological or not), which performances are well understood and with few challenges associated with the integration.

Sartor and collaborators (2008) evaluated the potential application of a pre-ozonation + MF/UV-GAC filter to treat surface water in Thailand. The GAC post-treatment was deemed essential to remove dissolved organics by adsorption (> 87 %) in order to achieve biological stability of the treated effluent.

Niquette et al. (2007) operated a pre-ozonation + MF + biological GAC process for over a 16 week period on a highly colored (5 - 8 mg C/L) river water in Quebec (Canada). The DOC measured in the biological GAC filter effluent progressively rose from 0.5 to 4 mg C/L after 5 weeks (adsorption mode) and roughly maintained this performance for the remainder of the study (biological mode). Even at 2°C, the THMFP measured as SDS-THM, was high (≈ 70 µg/L). This removal efficiency (≈ 50%) was the combined result of ozonation and biological GAC filtration. In addition, it is questionable if this process could meet THMs regulations under warm water conditions considering the DOC concentration that remains in the effluent. Schlichter and collaborators (2004) demonstrated that the performance of this post-treatment configuration could only meet DBP regulations if organic matter could be lowered to 2 mg C/L in the membrane permeate. Finally, as for biological GAC filters, the risk of increasing the microbial load at the effluent of the HMP can raise some concerns, mainly with respect to the release of bacteria in suspension or attached to AC fines (Prévost et al., 2005). While studies demonstrated that the release of bacteria in suspension can be controlled by efficient post-filter disinfection (LeChevallier et al., 1992; Najm, 2000; Suffet, 1980), the release of fines can be responsible for more issues (Camper et al., 1986). The risk to public health appears limited for fines colonized by heterotrophic bacteria (Morin et al., 1996). However, other pathogens (e.g. opportunistic pathogens) can colonize AC fines (Camper et al., 1986; Stewart et al., 1990) and it has been demonstrated that bacteria developing on PAC surface are protected against disinfectants such as chlorine or chloramine (Stewart et al., 1990). Consequently, even if documented outbreaks have not been linked to the exportation of carbon fines from GAC filters, their release should be minimized through proper operation of filters (e.g. backwashes, cleaning of underdrains, etc.) (Prévost et al., 2005).

1.3.3.2 Impact of the operating conditions

As previously discussed for the other configurations, pre-ozonation is essential to enable effective removal of DBPs precursors for an activated carbon post-treatment layout by cleaving the molecules precursors of DBPs. Another effective solution to remove DBPs precursors as well as organic matter is pre-coagulation. Yet, in the absence of coagulation, the performance of the process will depend highly on the ability of the activated carbon step to adsorb the DOC. Indeed,

Müller et al. (2009) integrated a coagulation step prior to the UF to enhance the trace contaminants removal.

There are three advantages associated to the activated carbon post-treatment configuration. First, placing a CC after the membranes will improve the overall treated water quality. Secondly, it will act as a protection for the treatment in case of any breakage of the membranes. Thirdly, when a GAC filter is placed after the membranes, the removal of turbidity during the membrane filtration may help to extend the GAC bed life and filtration cycle.

1.4 Fouling in HMP

Fouling may result from pore constriction, pore blocking, formation of a cake layer and/or a gel layer on the membrane surface and, in certain cases, biofouling. Typically, the main resistance to membrane flux lies in the development of a cake layer (Seo et al., 2005). Particulate matter such as clay, silt or virgin PAC does not contribute significantly to fouling on its own (Li et al., 2004). Deposited on the membrane surface, it forms a cake layer which leads to reversible fouling (removable by backwashing). However, NOM can lead to significant hydraulically irreversible fouling (Combe et al., 1999; Kaiya et al., 1996) and even chemically irreversible fouling (Oh et al., 2006). Dissolved organic matter, especially colloidal matter from 3 to 20 nm, humic substances and biopolymers are the main contributors to membrane fouling (Combe et al., 1999; Costa et al., 2006; Crozes et al., 1993; Kennedy et al., 2008; Li et al., 2004; Lin et al., 1999; Tomaszewska et al., 2002; Yuan et al., 1999, 2000). Fouling also depends on the physical and chemical properties of the membrane (in particular its hydrophilicity (Campinas et al., 2010a)) as well as on the operating conditions of the process (Crozes et al., 1993; Crozes, Marshall, et al., 1997; Hong et al., 1997; Kim et al., 2007; Kim et al., 1996; Kim et al., 2008; Mozia et al., 2005). Research indicates that hydrophilic membranes are generally better suited for filtration of surface water (Crozes et al., 1993; Crozes, Marshall, et al., 1997; Seo et al., 2005). For the need of the current review, discussion on fouling will be limited to the beneficial/detrimental role of PAC and the strategies to mitigate fouling in the HMP.

1.4.1 Role of PAC in membrane fouling

1.4.1.1 Impact of PAC on clean water permeability

Laboratory tests have been conducted with distilled water spiked with PAC in order to evaluate its impact on clean membrane permeability. Most of the authors agree that the permeability is minimally impacted by the addition of PAC (Campinas et al., 2010a; Mozia et al., 2005; Yiantsios et al., 2001). For example, Jones et al. (1993) assumed that the flux was not affected by the porous cake layer formed by PAC at the surface of the membrane. In preliminary tests, studies demonstrated that PAC addition to pure water may even improve the permeability (Lin et al., 1999; Mozia et al., 2006). In case of clean membrane in contact with PAC, the increased permeability could result from the abrasion effect of PAC and the following loss of membrane integrity. However, this hypothesis was not supported by Mozia et al. (2006). They observed that the increase in water permeability (50%) was not related to any decline in the separation properties of the membrane. Consequently, they assumed that the abrasion contributed to the opening of inactive pores, enhancing the permeability of the membrane. Other research led by Pirbazari, Badriyha and Ravindran (1992) assumed that the PAC deposition on membrane surface was responsible for the reduction of the boundary layer thickness and a consequent increase in the mass transfer coefficient, leading to higher permeate fluxes. Contradicting results were reported by Tomaszewska et al. (2002) who observed a significant decrease in membrane permeability (46%) as a result of PAC addition (50 mg/L). The authors suggested that the extent of fouling could be dependent on the type of PAC, the operating conditions and the membrane material. Operating under an adsorption strategy, it has been recommended to use a narrow size distribution along with a PAC size 100 times bigger than the pore size to reduce eventual pore plugging (Saravia et al., 2006).

1.4.1.2 Impact of PAC on membrane fouling in presence of NOM.

Literature review demonstrated that PAC allows controlling irreversible fouling by removing a fraction of the organic matter (Campinas et al., 2010a; Jacangelo et al., 1995; Kim et al., 2007; Kim et al., 1996; Oh et al., 2006; Ravindran et al., 2009; Song et al., 2009; Suzuki et al., 1998; Tomaszewska et al., 2002; Zhang et al., 2003). However, other studies have reported the opposite (Campinas et al., 2010a; Jacangelo et al., 1995; Oh et al., 2006; Seo et al., 2005; Zhang et al., 2003; Zhao et al., 2005) and demonstrated that PAC can be responsible for reversible fouling

(Jacangelo et al., 1995; Mozia et al., 2004). These contradicting results are likely due to the complex interactions between NOM, PAC particles and membrane surfaces. Firstly, PAC can preferentially adsorb non-foulant NOM fractions over foulants (i.e. PAC not effective to remove NOM < 300 kDa and > 17000 kDa) (Kim et al., 2008; Lee et al., 2005; Li et al., 2004; Lin et al., 1999). Secondly, although the presence of PAC increases the porosity of the cake layer (Adham et al., 1991; Khan et al., 2009; Mozia et al., 2004; Xia et al., 2007), which should therefore limit the loss in permeability (Mozia et al., 2004), PAC can form a more complex continuous cake layer at the membrane surface due to interactions with NOM, the biomass and the metal ions (Gai et al., 2008; Oh et al., 2006; Saravia et al., 2008; Seo et al., 2005; Zhang et al., 2003; Zhao et al., 2005). This results in a higher resistance to filtration. Thirdly, membrane fouling may be impacted by PAC characteristics. In a biological strategy, biofilm developing on PAC favors its adhesion on membranes resulting in significant major fouling (Seo et al., 2005). Finally, influent water quality can interact with NOM. For example, Yiantsios et al. (2001) demonstrated that calcium precipitation reduced flux while Song et al. (2009) observed that β-estradiol could interact with NOM and accelerate fouling. Pretreatments can be used to modify water quality, to alleviate fouling, keeping in mind that pretreatment themselves can increase fouling in the presence of PAC. For example, the impact of coagulation on fouling depends on the type of coagulant used, the dose of coagulant applied, the type of matrix treated as well as on the type of membrane used (Howe et al., 2006). Consequently, an optimal PAC concentration likely exists for which the increase in resistance caused by PAC particles are offset by the reduction of fouling due to NOM (Kim et al., 2007). However, this ability to reduce fouling can be overwhelmed by the formation of a dense layer, leading to an overall increase in fouling (Zhang et al., 2003). Therefore, at this point, more research is needed to define this optimum which is probably not only system-specific but also seasonally-dependent.

1.4.2 Fouling mitigation

1.4.2.1 HMP with pre- or integrated activated carbon treatment

PAC size. In case of contact between PAC and membranes, PAC size has to be optimized. According to Zhao et al. (2005), larger PAC (around 150 µm) offers larger void space and particle size distribution, a characteristic which favors interactions with colloidal matter and metal ions and, consequently, more intense PAC cake fouling. However, in the adsorption mode,

the decrease of PAC particle size down to the pore size of the membrane was observed in high shear forces conditions (Londono Montoya et al., 2011). Khan et al. (2011) noticed that the reduction of PAC size was associated to the reduction of the size of the suspended solids (SS) entering the process. This interaction between SS and PAC led to reduction of fouling. However, while observing PAC size reduction, a recent study demonstrated that PAC could be facilitating the adsorption of organic and inorganic foulants onto the membrane (Londono Montoya et al., 2011). In the biological mode, Markarian et al. (2010) observed, when comparing 25 µm and 200 µm PAC, that PAC size progressively becomes larger during colonization. This increase of PAC size led to the increase of its settleability. This change in PAC size would facilitate PAC separation from the water to be treated by the membranes.

Selection of the operating flux. As with any membrane system, a compromise has to be found while operating a HMP between productivity and membrane fouling, fouling monitoring being mostly done through transmembrane pressure (TMP) control. It has often been demonstrated that low fluxes values minimize fouling and enhance operation efficiency through the reduction of the extent of fouling and an increased contact time between activated carbon and water (Crozes, Jacangelo, et al., 1997; Jia et al., 2009; Kim et al., 2007; Lebeau et al., 1998; Seo et al., 2005; Seo et al., 2004; Vigneswaran et al., 2007). However, operating with an elevated PAC concentration (40 g/L) can lead to short period of operation of the membranes (2 months) (Khan et al., 2009) and thus frequent membrane replacement (Seo et al., 2004). By regulating TMP under a threshold value, specific to the influent water, it is possible to limit irreversible fouling (Crozes, Jacangelo, et al., 1997). For a system operated with 20 g/L of biological PAC, the critical flux, described as a threshold above which the fouling rate increases drastically (Seo et al., 2004), has been reported to range from 15 to 30 L/(m^2.h) in the biological mode (Barbeau et al., 2011; Barbeau et al., 2010). The critical flux for hybrid systems has thus been reported to be similar to that for MBRs used in wastewater treatment, and lower that for membrane systems used for drinking water treatment.

Mode of operation. For three types of PAC dosed at 10 mg/L, Saravia et al. (2006) did not observe any flux decline on MF membranes operated in crossflow. The performances were also independent of PAC particle size distribution (Saravia et al., 2006). The lack of fouling was attributed to the abrasion of the fouling layer by PAC (Saravia et al., 2006). This scouring effect was observed by Oh et al. (2006) to increase as the concentration of larger particles in the

concentrate. In crossflow operation (0.5 m/s), high PAC concentrations (288 – 576mg/L) could even enhance membrane flux (Campos et al., 1998). These authors observed that PAC did not impact reversible and reduced irreversible fouling. However, the scouring effect does not always happen. The crossflow velocity (CFV) and the pressure highly influence this phenomenon (Jacangelo et al., 1995). In addition, PAC particles could be too light to interact with the film layer at the membrane surface (Jacangelo et al., 1995). Implementing a turbulent flow regime could enhance the scouring of the fouling layer by PAC (Pirbazari, Badriyha, Kim, et al., 1992). At industrial scale, CFV value typically range from 0.5 to 1 m/s. As reviewed by Belfort et al. (1994), at low solids (e.g. PAC) concentrations and/or permeate flux, the convective flow of material towards the membrane is low. Therefore, increasing the CFV or extent of turbulence, which increases the mass flux of foulants away from the membrane surface, does not significantly affect the overall rate of fouling. However, when the convective flow of material towards the membrane is high (i.e. at high solids concentrations or high permeate flow), the rate of foulant accumulation can be significantly reduced by increasing the CFV or extent of turbulence. These observations were confirmed for the HMP. At a low PAC dosage of 5 mg/L, Campinas et al. (2010a) did not observe reduced fouling after increasing CFV from 0.5 to 1.0 m/s. Crozes, Marshall, et al. (1997) demonstrated that CFV did not impact flux when the later was low (e.g. 35 L/(m^2.h)). However, at high flux (e.g. 110 L/(m^2.h)), a CFV of 0.9 m/s was insufficient to maintain PAC in suspension. Jacangelo et al. (1995) also concluded that for a given membrane flux, PAC concentration had a stronger impact on TMP at lower CFV. Although crossflow filtration may allow higher permeate flux with reduced fouling when using high doses of PAC, its application increases energy costs and, from a water quality perspective, does not enhance the efficiency of the process (Matsui et al., 2001). In addition, some concerns could be raised concerning the potential loss of integrity of the membranes due to its abrasion by PAC. This effect would depend on the type of PAC, the type of membrane used and on the operating conditions of the process. An alternative to crossflow filtration to enhance water production is to avoid the contact of PAC with the membrane. By implementing a separation step, fouling could be reduced substantially. The ACTIFLO^{TM} CARB process is a high rate ballasted settler (using microsand/polymer/coagulation) which allows PAC recirculation. Settled PAC is separated by a hydrocyclone. To the best of our knowledge, this is the only example of full-scale application of this concept.

Backwashes. Backwashes are largely employed to manage membrane fouling (Hilal et al., 2005). Backwash conditions can be defined with regards to their frequency, their intensity, their duration and the use or not of a dual phase (air/water) (Khan et al., 2009; Vigneswaran et al., 2007). Concerning the HMP, the implementation of a quick flush after the backwash of inside-out fibers could enhance the removal of deposited PAC (Adham et al., 1991; Campinas et al., 2010a). However, the optimum of the backwash conditions that would permit an optimal restoration of the permeability of the membranes and an extended operational period is most likely system-specific. Additional research is needed in this area considering the significant impact on the operational costs. For example, the integrated activated carbon configuration (the worst case scenario for fouling) has been operated with backpulses every 10-15 min (Lebeau et al., 1998; Treguer et al., 2010) which may last for 1-2 min. This represents a significant loss of productivity.

Aeration. In the integrated configuration, aeration appears to prevent fouling by reducing the aggregation of PAC particles to the membrane (Khan et al., 2009; Khan et al., 2011). However, Seo et al. (2005) and Barbeau et al. (2010) both observed that aeration was less effective at reducing fouling when PAC turned from adsorption to biological mode.

Chemical cleaning. Chemical cleaning is also used to manage fouling. In the presence of PAC, it is our opinion that cleaning-in-place procedures should be revisited. For one, the presence of PAC in the cake layer will increase chlorine demand. It might also be advisable to perform a physical cleaning prior to the cleaning-in-place in order to remove as much PAC as possible.

1.4.2.2 HMP with activated carbon post-treatment

In this type of configuration, the mitigation of membrane fouling is not specific to the hybrid process and consequently, readers are referred to other reviews (Hilal et al., 2005).

A pre-treatment step is typically employed to reduce membrane fouling. Coagulant dose and type impacts the permeability of the membrane. Ozonation pretreatment was demonstrated to reduce backwash frequency (Niquette et al., 2007). The remaining fouling can be mostly reversed and practically removed with each backflushing cycle (Sartor et al., 2008). However, most membranes do not tolerate well ozone and, therefore, this strategy must be used cautiously (ozone quenching) or using ozone-tolerant membranes.

1.5 Discussion and conclusion

The use of the HMP has been the topic of many investigations as over 30 publications were found on the subject in the scientific literature. Clearly, from a water quality perspective, the anticipated performance can be quite high, especially while operating under the adsorption mode. Research performed using PAC in the biological mode is more limited but are indicative that this process may be as efficient as biological GAC filters and less expensive than PAC in the adsorption mode. The selection of one strategy over another will be based on the influent water characteristics and the water quality regulation in place. Strict regulations on pesticides, such as what is observed in Europe, would clearly favor the adsorption mode. The interesting aspect of the HMP processes using PAC is that switching from one mode of operation to another is straightforward. Therefore, a utility could elect to vary their strategy seasonally or following a revision of water quality regulations.

At this point in time, most HMP processes that have been built at industrial-scale have avoided the contact of PAC with the membranes. Clearly, managing the interaction of PAC with the membrane remains a challenge. The most notable exception is the CRISTAL^{TM} process. However, the PAC concentration in contact with the membrane is fairly low in comparisons with other HMP alternatives. The integrated HMP configuration offers the advantage of a more compact process. It could also be an easier solution to implement in existing vacuum-driven membrane systems or conventional treatment plants. However, more research is needed to properly design the membrane modules and adequately manage the formation and backwash of the PAC cake layer. Both will impact process productivity and will dictate if, ultimately, it is preferable to separate both unit processes even at the cost of adding an additional unit process to recycle the PAC in the CC. In addition, under biological mode, there may be a need to manage the accumulation of suspended solids inside the reactor. In the area of MBR application for wastewater treatment, the accumulation of inert material in the mixed liquor has been reported to negatively affect the MBR efficiency (Han et al., 2005). Finally, in the crossflow filtration mode, the issue of PAC abrasion on the membrane has received little attention as most pilots were conducted for short periods of time or with relatively low PAC concentrations (i.e. in the order of mg/L). Abrasion might be an additional reason for avoiding the direct contact of PAC with the membrane if high PAC concentration is required (i.e. in the order of g/L).

The HMP with an activated carbon pre-treatment configuration resolves most of the fouling issues if a separation step is used. Yet, the application of this process is more complex if powdered rather than granular activated carbon is employed. Ultimately, the use of PAC (or fluidized GAC) appears as a more interesting approach as it offers the possibility to adjust treatment based on water quality. The use of the HMP with an activated carbon post-treatment is already quite common in the water industry. The advantage clearly lies in the fact that the influent of the CC will be free of particulate matter. This characteristic should improve treatment performance both in the adsorption or biological mode. However, questions remain as if this improvement of treatment performance surpasses, from an economical and operational perspective, the potential control of fouling obtained by placing the CC ahead of the membrane. In addition, this configuration is limited to using GAC filters as CC in order to avoid the release of PAC fines in the finished water.

In conclusion, finding the optimal alternative for the combination of activated carbon and LPM remains a challenge for the HMP. Pre- and integrated activated carbon treatment layouts both offer high potential to efficiently treat polluted surface waters. Although operating conditions still require to be optimized (e.g. PAC concentration, PAC age, filtration cycles), some configurations are already commercially available and we expect that many full-scale applications will be built in the next decade. Clearly, the future of this process lies in (i) the regulatory push that may impose higher trace contaminant removal and (ii) the process development of alternative treatment technologies, such as nanofiltration. Future research comparing both treatment strategies (HMP and NF) from an environmental as well as an economical life-cycle cost should be conducted.

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CHAPTER 2 RESEARCH OBJECTIVES, HYPOTHESES AND METHODOLOGY

2.1 Critical review of previous research

HMPs, coupling the usage of PAC with low-pressure membrane filtration stand out as a promising alternative to conventional drinking water treatment (coagulation/flocculation + sedimentation + filtration), as suggested by the rising number of publications on the topic. The latest developments in HMPs are presented in the published literature review (Stoquart et al., 2012). Chapter 1 highlights the potential of the HMPs using aged PAC but also the lack of data, which hinders a thorough understanding of the process resulting in sub-optimal usage of the carbon contactor at high PAC residence times.

Most of the published studies on HMPs use the PAC as adsorbent (< 7 days, referred to as the adsorption mode in Chapter 1). Operating the HMP with a low PAC residence time allows for important decreases in NOM concentration (median of 70% across the literature, see Chapter 1) and micropollutant concentration (hormones, herbicides, etc.). In contrast, the potential for ammonia removal of HMPs using low PAC age was not investigated, most likely due to low efficiency expectations. However, the remaining ammonia concentration may lead to taste and odor issues after chlorination as well as to an increased chlorine demand. Applying higher PAC age in HMPs (referred to as biological mode in Chapter 1) emerges thus as a promising alternative to reach the simultaneous removal of NOM and ammonia, with the additional benefit of reducing the operational and environmental cost of the process by minimizing fresh PAC consumption. However, micropollutants constitute an increasing preoccupation in water treatment as they are detected in wastewater effluents (Miège et al., 2009), source waters (Huerta-Fontela et al., 2011) and drinking water (Coupe et al., 2004). The potential for micropollutants removal in HMPs using aged PAC is still unknown. To the best of our knowledge, the only published studies evidencing the adsorption potential of aged PAC in HMPs demonstrated that atrazine was adsorbed on 60-d PAC (Lebeau et al., 1998; Lebeau et al., 1999).

If HMPs are operated with aged PAC (> 7 days), the colonization of the PAC by both nitrifying and heterotrophic bacteria is expected. Letting PAC age in the HMP would thus lead to a shift from an adsorptive treatment towards a biological treatment, with nitrification and biodegradation

of the NOM occurring in the PAC contactor. The relative importance of these mechanisms would be tied to the age of the PAC. The colonization of the PAC was suggested based on the maintained 20% removal attributed to DOC biodegradation after complete exhaustion of the adsorption capacity (Seo et al., 2004), the increase in BDOC removal with PAC age (Léveillé et al., 2013) and the increase in ammonia removal with PAC age attributed to the colonization by nitrifying bacteria (Seo et al., 2004; Suzuki et al., 1998). Yet, there is currently no existing method to quantify the bacterial biomass on PAC. In addition, several authors mentioned that HMPs' performance could be attributed to a combination of adsorption and biodegradation. However, these studies were mainly done on membrane bioreactors to which virgin PAC was added (Williams et al., 2007) or in HMPs where PAC is aged and never replaced, and therefore the adsorption capacity is gradually exhausted (Seo et al., 2002; Seo et al., 2004). Under steady-state operation of HMPs, the PAC age is maintained constant by a systematic purging and replenishment of a fraction of its mass. Therefore, for compounds amenable to biodegradation and adsorption (e.g. biodegradable DOC, BDOC), although the biological activity is expected to be mostly responsible for their removal when using aged PAC, a residual adsorption capacity cannot be discarded. However, no published study ever set out to discriminate the respective roles of adsorption and biodegradation in the PAC contactor of an HMP operated at steady-state with aged PAC. Yet, knowing the relative importance of adsorption and biodegradation for the removal of compounds of interest is necessary in order to establish operating guidelines to optimize the process.

Finally, the majority of the published research on HMPs using aged PAC corresponds to pilot-scale studies that evidenced:

i) the potential of the process in ammonia (Kim et al., 2005; Seo et al., 2002; Suzuki et al., 1998) and DOC removal (Lebeau et al., 1998; Treguer et al., 2008)

ii) the low importance of the PAC size under high PAC residence time (Markarian et al., 2010),

iii) the increase in water quality with increased PAC concentrations (Kim et al., 2005; Markarian et al., 2010),

iv) the decrease in efficiency with increased activated carbon age (Kim et al., 2009; Seo et al., 2004; Suzuki et al., 1998),

v) the potential gains from increasing the HRT from 15 to 30 min (Markarian et al., 2010).

Seasonal temperature variations such as the ones in Canada are expected to impact the performance of HMPs, as both adsorption and biodegradation are likely influenced by temperature. Optimal operating conditions will thus vary strongly with seasonal changes and studying the HMP using aged PAC under colder temperature is crucial to an optimized operation. Yet, most of the published studies on aged PAC were realized under warm water conditions. Little was published on the impact of temperature drops on the quality of the treated water.

In summary, the weaknesses of the current research on the HMP operated with aged PAC are the following:

1) Colonization of aged PAC by heterotrophic and nitrifying biomass was suggested but never quantified;
2) Mechanisms responsible for dissolved compound removals occurring on aged PAC were never studied. Discrimination between these mechanisms is lacking;
3) Potential of the HMP using aged PAC was studied under warm water temperature. Little information was published under cooler conditions;
4) Potential of the HMP using aged PAC to remove micropollutants is poorly studied;
5) The operation of HMPs using aged PAC remains to be optimized.

2.2 Objectives

The general objective of this research project is to describe the performance of the PAC contactor of HMPs in removing ammonia, DOC, BDOC and micropollutants. In particular, emphasis is placed on the operation of the HMP using aged PAC.

On a more detailed level, the objectives of this project are to:

1. Develop and compare methods to quantify the biomass developed on aged PAC;
2. Develop a method to produce an abiotic control for aged PAC;
3. Characterize the removal kinetics of ammonia, DOC, BDOC and micropollutants occurring in the carbon contactor of an HMP;

4. Evaluate the impact of the water temperature on the performance of the carbon contactor of an HMP;
5. Discriminate the relative importance of adsorption versus biological oxidation as mechanisms responsible for ammonia, DOC and micropollutants removal in the PAC contactor of an HMP;
6. Differentiate the relative importance of the HRT, the PAC age and the PAC concentration as key operating parameters on the optimization of the performance of the PAC contactor of an HMP.

Addressing these objectives will allow us to conclude on the following aspects:

- Does the residual adsorption capacity of aged PAC suspensions contribute significantly to the performance of the HMP for ammonia, DOC and micropollutants removal?
- Amongst the PAC age, the PAC concentration and the HRT, is there a key parameter in the operation of the HMP for ammonia, DOC and micropollutants removal?

The hypotheses that ground the objectives of this project are the following:

1. Active heterotrophic and nitrifying bacteria colonize the PAC in the contactor of an HMP operated at steady-state with mean PAC ages of 10 days and 60 days.

   Originality: There is no existing method that allows to evaluate the biomass colonizing the PAC.

   This hypothesis will be proven wrong if the heterotrophic biomass detected on aged PAC is not at least ten times higher than on the abiotic control and if there is no nitrite and nitrate production associated to the ammonia concentration depletion.

2. It is possible to define an optimized dose of gamma-rays that inhibits the active biomass of a colonized PAC without significantly altering its adsorptive properties.

   Originality: Gamma-irradiation is a common sterilization practice and is efficient to produce abiotic controls for soil samples. However, it has never been tested for the purpose of inhibiting the activity of heterotrophic bacteria fixed on colonized PAC.

This hypothesis will be proven wrong if the bacterial activity on the irradiated colonized PAC is not significantly decreased ($p>0.05$) or superior to 20% of the initial bacterial activity and/or if the adsorption capacity and/or adsorption kinetics were significantly altered ($p<0.05$) by the gamma-irradiation.

3. Ammonia removal on colonized PAC is due to the nitrifying activity of the autotrophic biomass. Ammonia adsorption on colonized PAC is negligible.

   Originality: Ammonia removal mechanisms on colonized PAC were never investigated. Ammonia adsorption on activated carbon has always been assumed to be negligible.

   This hypothesis will be proven wrong if ammonia adsorption is significant ($p<0.05$) or if it is responsible for more than 10% of the total ammonia removal.

4. DOC removal in the PAC contactor of an HMP is due to a combination of its adsorption onto PAC and its biodegradation by the heterotrophic biomass developed on the PAC.

   Originality: The fraction of DOC removal attributed to the residual adsorption capacity of a colonized PAC is unknown.

   This hypothesis will be proven wrong if DOC adsorption and/or DOC biodegradation onto colonized PAC is not statistically significant ($p>0.05$) or is marginal (less than 10%).

5. Natural organic matter biodegradation and nitrification kinetics on colonized PAC follow a Michaelis-Menten law, of which the parameters are affected by water composition and temperature.

   Originality: Biodegradation and nitrification kinetics were never characterized in the carbon contactor of an HMP.

   This hypothesis will be proven wrong if the Michaelis-Menten law is not verified and/or if the temperature is not a key operating parameter for the biodegradation kinetics of BDOC and/or ammonia.

6. A residual adsorption capacity on aged PAC is responsible for significant micropollutants removal in an HMP.

   <u>Originality:</u> Few studies were published on micropollutants removal in HMPs operated at high PAC residence time. Micropollutants removal kinetics in the carbon contactor of an HMP are unknown.

   This hypothesis will be proven wrong if no significant micropollutants removal is noted on 10-d and 60-d PAC ($p>0.05$)and/or if micropollutants removal on aged PAC and its corresponding abiotic control is significantly different ($p>0.05$).

7. The PAC age, the PAC concentration and the HRT are operating parameters to consider for the optimized operation of the HMP.

   <u>Originality:</u> The role of the PAC age, PAC concentration and HRT has not been extensively investigated.

   This hypothesis will be proven wrong if any of these three parameters does not affect significantly the performance of the HMP for the removal of the targeted compounds (ammonia, DOC and micropollutants)($p>0.05$).

2.3 Methodology

In this research project, operating the HMP with aged PAC was investigated. In particular, emphasis was placed on the mechanisms responsible for dissolved compounds removal by PAC, as well as on the impact of various operating parameters on the performance of the PAC contactor. The present project is divided in two phases. Phase 1 addresses objectives #1 and #2. It corresponds to the methodological developments necessary to set the basis on the study of aged PACs: the development of methods i) to quantify the heterotrophic and nitrifying biomass developed on aged PAC and ii) to create a reliable abiotic control of the colonized PAC, which is required for discriminating the mechanisms occurring on aged PAC. Phase 2 addresses objectives #3 to #6. It evidences the potential efficiency of the HMP for the removal of ammonia, DOC and a mixture of micropollutants. The removal kinetics were monitored over a variety of operating conditions. Models were developed based on the kinetics monitored at lab scale to predict ammonia and DOC removal in the PAC contactor of an HMP. Based on lab-data and models, i) the mechanisms responsible for the dissolved compounds removal were discriminated, ii) the

relative importance of the major operating parameters of the PAC contactor of an HMP for the various compounds targeted was determined and finally, iii) the knowledge of the behavior of a suspension of aged PAC in HMPs was broaden.

The methodology applied is presented in the following sections. Section 2.3.1 presents the HMP pilot-plant utilized for the production of aged/colonized PAC. The methodology developed during phase 1 of the project is described in section 2.3.2 and section 2.3.3 describes the methodology of phase 2.

2.3.1 Pilot-plant operation

2.3.1.1 Hybrid membrane process pilot-plant

An HMP pilot-plant was run to produce the aged PAC utilized in this project. The pilot-plant was installed in the facilities of the Ste-Rose DWTP in the city of Laval (Qc, Canada). An overview of the pilot-plant is presented in Figure 2-1a). The pilot-plant includes two of the configurations presented in Chapter 1: i) an integrated activated carbon HMP (i.e. Opaline B®, see Figure 2-1b) and ii) an HMP with an activated carbon pre-treatment (i.e.Opaline S®, see Figure 2-2). Each configuration includes two identical treatment chains. The four PAC contactors were fed in parallel by the same settled water from the Ste-Rose DWTP (pH = 6.70 ± 0.11; turbidity = 0.62±0.40 NTU; UV254 = 0.056±0.007 cm^{-1}; DOC = 3.02±0.30 mg C /L; BDOC=0.27±0.11 mg C/L, alkalinity = 20±2 mg $CaCO_3$/L).

Opaline B®. Besides the two PAC contactors with immerged membranes, the integrated pilot-plant (see Figure 2-1b) also includes additional tanks to empty the PAC contactor, to prepare the virgin PAC for dosages and to gather the permeate. The immerged PAC contactor included an aeration system, which i) maintained the oxygenation of the contactor, ii) maintained the mixing of the PAC suspension and iii) reduced the membrane fouling (Charest, 2009). In both reactors, the colonization of the PAC was realized similarly. A fixed mass of PAC was added in the contactor. The PAC suspension was aged without any purges or replacement of virgin PAC until the targeted PAC age was reached. The PAC age was then maintained by purging and replenishing daily a fraction of the mass of PAC in the carbon contactor. Characteristics of the operation of the Opaline B® pilot-plant are presented in Table 2-1. The pilot-plant was operated for a total of 431 days between the winter of 2011 and the summer of 2012.

a) b)

Figure 2-1 : Views of a) the entire pilot-plant and b) the Opaline B® section of the pilot-plant

Opaline S®. In this configuration, two stirred reactors were filled by a PAC suspension (Figure 2-2a). The entire mass of PAC was maintained in the contactors by a 55-85 µm sieve (Figure 2-3). At the time of sampling, the pressurized membranes modules were not functioning (Figure 2-2b). This did not have any impact on the present project as the 55-85 µm sieve retained the PAC in the contactor. During this study, the contactors were operated continuously, without any PAC replacement or purges. The PAC contactors of the pilot-plant were operated for 67 days. Characteristics of the operation of Opaline S® pilot are presented in Table 2-1.

a) b)

Figure 2-2 : View of a) the PAC contactors and b) the separated pressurized membranes in the Opaline S® section of the pilot plant.

a) b)

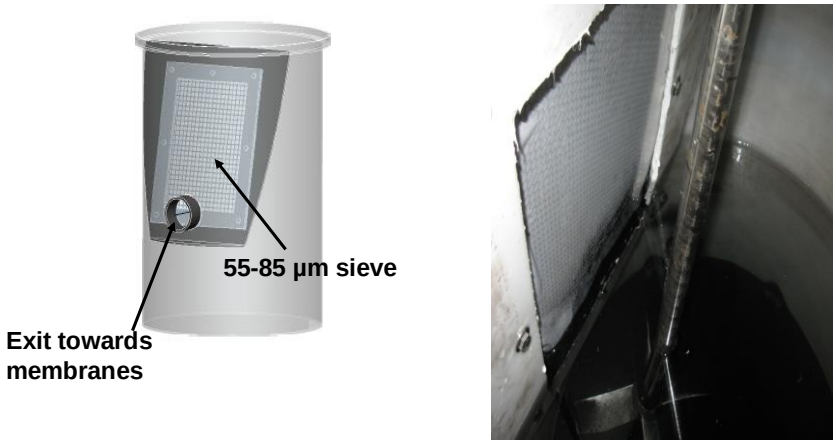

Figure 2-3 : Schematic (a) and View (b) of the 55-85 µm sieve in the PAC contactors of the Opaline S® section of the pilot-plant

Table 2-1: Operational characteristics of the pilot-plants

Parameters	**Values**	
PAC contactor	Opaline B®	Opaline S®
PAC type	Picahydro® LP39	Picahydro® L30-260
PAC mean age	Reactor 1: 60-d Reactor 2: 10-d	67-d
PAC concentration (dry weights)	Reactor 1: 9.8±1.1 g/L Reactor 2: 3.5±1.2 g/L	Reactor 1: 1.2±0.0 g/L Reactor 2: 5.5±0.2 g/L
Volume	173 L	200 L
Diameter/height	0.35m/2.1m	0.64m/0.62m
Aeration rate	37 L/min	Mechanical agitation @ 200rpm
Hydraulic retention time	67 min	30 min
Membranes		
Flux	25 LMH	0 LMH
Membrane area	10 m²/reactor	3.6 m²/reactor (type 1) 2.2 m²/reactor (type 2)
Membrane type	PES hollow fibers (Puron)	Type 1: PES hollow fibers (Norit) Type 2: Titanium oxide Honeycomb (CeraMem)
Porosity[a]	0.05 µm	Type 1: 0.025 µm Type 2: 0.1 µm

[a]according to the supplier

2.3.1.2 Powdered activated carbon

The same PAC was used during the entire project. The PAC chosen is wood-based, chemically activated and commercialized by Pica™. The Opaline B® pilot-plant was operated with PAC presenting a mean diameter of 24 µm and a median of 18.7 µm (picahydro® LP39). For separation purposes, the Opaline S® pilot plant was operated with the same PAC but presenting a

larger grain size (mean diameter of 210-260 µm, picahydro® L30-260). A larger grain size was required for separation purposes. The chemical activation of the Pica™ PAC creates meso- to macro-pores. This type of activated carbon was demonstrated to be best suited for the development of a biological process (Yapsaklı et al., 2009). Indeed, while the smaller pores of a microporous PAC are extremely efficient for adsorbing small molecules such as pesticides (Ebie et al., 1995), the larger pores allow bacteria to settle in and be protected from external shear forces (Wang et al., 1995).

The aged PAC studied in the papers constituting Chapter 3 to Chapter 7 was mainly the picahydro® LP39 aged in the Opaline B® pilot plant. As the Opaline B® pilot plant was operated at steady-state, the usage of its PAC allowed monitoring removal kinetics on an aged PAC that was representative of the full-scale operation of an HMP. The Opaline S® pilot plant was used for the purpose of colonizing a larger amount of PAC when developing the biomass quantifying methods (Chapter 3).

2.3.2 Phase 1: Methodological aspects

2.3.2.1 Objective #1: "Develop and compare methods to quantify the biomass developed on aged PAC" (Hypothesis 1)

Heterotrophic biomass

Lots of methods exist to quantify the biomass present at the surface of colonized granular activated carbon (GAC) from BAC filters. In this project, several of these methods were adapted from GAC to PAC. Heterotrophic plate counts (HPC) (American Public Health Association (APHA) et al., 2012) and bacterial ATP measurements (Profile®-1 Reagent Kit, New Horizons Diagnostics, USA) required the detachment of the biomass from the activated carbon (Camper et al., 1985a), with the drawback of potential incomplete recovery and/or degradation of the bacterial cells during detachment (Lazarova et al., 1994). Exopolymeric substances (EPS: proteins and polysaccharides) were extracted from colonized activated carbon (Liu et al., 2002). The potential ^{14}C-glucose respiration (PGR) rate quantifies the active heterotrophic biomass by evaluating the maximal respiration rate of ^{14}C-glucose through the detection of radio-labeled carbon dioxide (Servais et al., 1991). This method appears to be the most favorable, as biomass recovery or degradation problems are avoided. However, the usage of radio-labeled products is

expensive and can cause logistical issues. Another method targeting the quantification of active biomass was therefore developed. It is based on the measurement of potential acetate uptake (PAU) rates. Acetate was chosen as a substrate because it is ubiquitous, readily biodegradable and not adsorbable on PAC (Wang et al., 1995). PAU rates were measured by following acetate removal kinetics in PAC suspensions of 20 g/L (wet weight) at 20°C. Acetate biodegradation kinetics is demonstrated to follow zero-order kinetics in saturating conditions, and the PAU rate is used as a proxy to quantify the biomass. All the cited methods (HPC, bacterial ATP, EPS, PGR and PAU) were conducted on 4 different colonized PACs as well as on biological GAC samples from a full-scale biological filter. PACs were colonized in the reactors of the Opaline B® and Opaline S® pilots. The biological GAC was gathered from the BAC filters of the Ste-Rose DWTP. All these methods were well correlated and demonstrated that colonized PAC presented a heterotrophic bacterial activity (per gram of AC) similar to that of BAC filters.

Nitrifying biomass

In BAC filters, the nitrifying bacterial biomass is indirectly evaluated based on the production rate of oxidized forms of nitrogen (i.e. nitrite and nitrate) in standardized optimal conditions (Kihn et al., 2000). This potential nitrifying activity (PNA) provides a proxy to evaluate the sum of ammonia- and nitrite-oxidizing bacteria. In this project, PNA method was adapted from biological GAC to PAC. The adaptation of the PNA method was straightforward and based on recovering a suspension of colonized PAC, gathering the colonized PAC, cleaning it with ammonia-free nitrifying medium and then applying the Kihn et al. (2000) method on 1 g wet weight of cleaned colonized PAC. The PNA method was applied on PAC samples from the Opaline B® pilot-plant. Both 10-d and 60-d PAC presented a PNA (per gram of AC) similar to that of BAC filters.

2.3.2.2 Objective #2: "Develop a method to produce an abiotic control for aged PAC" (Hypothesis 2)

The gamma-irradiation is used for soil sterilization and has been demonstrated to have a low impact on soil samples (Berns et al., 2008; McNamara et al., 2003). In this project, gamma irradiation was the chosen method to produce abiotic samples as it only targets the DNA of the bacteria. Therefore, the impact on the colonized PAC adsorption kinetics was expected to be lower than that of adding chemicals that might alter the ionic strength of the water matrix or

autoclaving the colonized PAC as it would alter the exopolysaccharides of the biofilm on the PAC (Berns et al., 2008), which in turn might affect the adsorption kinetics as biofilm hinders the diffusion (Fan et al., 1990). An adequate abiotic sample is expected to see its bacterial activity inhibited. Its adsorption characteristics must however remain unaltered. Colonized PAC suspensions were gathered from the pilot-plant and concentrated to 50 g/L. The concentrated suspension was exposed to gamma-rays with 6 incremental doses ranging from 0 to 25 kGy (C-188 60Co source, Underwater Calibrator-15A) in Nordion Inc. Facilities (Laval, QC, Canada). HPC were measured on the 6 irradiated PAC samples. This allowed us to determine the minimal dose of gamma-rays required to inhibit the growth of bacteria on agar plates (HPC method). Methylene blue (MB) was used as a non-biodegradable surrogate for organic matter (Ferreira-Leitão et al., 2007), as is the case in adsorption studies (Perry et al., 2005). MB adsorption kinetics on the irradiated PAC samples were modeled with a pseudo-second order (PSO) kinetics model. PSO modeling allowed evaluating the adsorption capacity at equilibrium (i.e. q_e) and the kinetics constant (i.e. k). The maximal gamma-ray dose was chosen as the dose limiting the impact of the irradiation on the parameters of the MB adsorption kinetics. In order to confirm the dosage chosen, PAU and PGR methods were conducted on a sample irradiated at the optimal dose. Both methods evidenced that gamma-irradiation drastically decreased the bacterial activity at the surface of the colonized PAC. Refractory DOC (RDOC) removal kinetics was monitored on both non-irradiated and irradiated colonized PAC to confirm the absence of alteration of the adsorptive behavior of the irradiated colonized PAC. The software Statistica 12 (Statsoft, USA) was used to demonstrate that the impact of the gamma-irradiation of the q_e- and k-parameters from the PSO model was not significant. Gamma-irradiation was therefore confirmed as a suitable method to produce abiotic PAC samples in this project.

2.3.3 Phase 2: Performance of the HMP

2.3.3.1 Objective #3: "Characterize the removal kinetics of ammonia, DOC, BDOC and micropollutants occurring in the carbon contactor of an HMP" (Hypotheses 3-6)

The same methodology was applied for all the dissolved compounds targeted (i.e. ammonia, DOC and micropollutants). Dissolved compounds kinetics removals were performed using suspensions of i) virgin PAC neutralized for 12-24h at pH =7 with a 1M NaOH solution and ii) aged PACs gathered from the Opaline B® pilot plant. Targeted mean PAC residence times for the

aged PACs were 10-d and 60-d. Both the virgin and the aged PAC suspensions were filtered and then resuspended in a chosen water matrix. The removal kinetics were conducted at a controlled PAC concentration. Dissolved compounds concentration depletion was monitored by sampling a fraction of the PAC suspension at increased contact times. The sample gathered was immediately filtered on a 0.45 µm PES filter (Supor-450, Pall® Corp., Ann Arbor, MI) to stop the contact between the water and the PAC. Dissolved compounds concentrations were then measured in the filtered samples. Operating conditions tested during the kinetics monitoring of this project are summarized in Table 2-2.

Table 2-2: Summary of the operating conditions tested

Ammonia removal kinetics					
Targeted contact time (min)	1, 5, 10, 15, 30, 60				
Water type	Settled water (SW)				
Initial ammonia concentration (μg N/L)	89 ± 20 984 ± 49				
Temperature (C)	7.2 ± 0.9 22 ± 1				
PAC age (d)	0 10 60				
PAC concentration (g dw/L)	1.0 ± 0.1 4.9 ± 0.4 9.7 ± 1.1				
DOC/BDOC/RDOC removal kinetics					
Targeted contact time (min)	1, 5, 10, 15, 30, 60				
Water type	Settled water (SW)			Raw water (RW)	
Ozone dose (g O_3/g C)	0	0.75 ± 0.11	1.38 ± 0.14	0	0.74 ± 0.05
Initial DOC concentration (mg C/L)	3.20 ± 0.41	3.05 ± 0.40	3.08 ± 0.35	7.17 ± 0.40	6.28 ± 0.53
Initial BDOC concentration (mg C/L)	0.30 ± 0.11	0.64 ± 0.14	0.98 ± 0.09	0.45 ± 0.12	1.60 ± 0.23
Initial RDOC concentration (mg C/L)	2.0 ± 0.44	2.42 ± 0.31	2.10 ± 0.32	6.72 ± 0.43	4.67 ± 0.41
Temperature (C)	7.2 ± 0.9 22 ± 1			7.2 ± 0.9	
PAC age (d)	0 10 60				
PAC concentration (g dw/L)	1.0 ± 0.1[a,b] 5.0 ± 0.8 9.7 ± 1.2[a,b,c]				

Note: Concentrations also tested with irradiated PAC at 7 C in SW[a] and in pre-O_3 SW[b] and in RW[c] and in pre-O_3 RW[c]

Table 2-2: Summary of the operating conditions tested (continue)

Micropollutants removal kinetics		
Targeted contact time (min)	1, 5, 10, 15, 45, 2h, 6h, 24h, 48h	
Water type	Settled water (SW)	
Ozone dose (g O3/g C)	0	0.85
Initial micropollutant concentration (µg/L)	Atrazine: 16.77 ± 1.57 DEA: 17.43 ± 1.66 Linuron: 15.91 ± 0.99 Caffeine: 2.23 ± 0.12 Sulfamethoxazole: 0.16 ± 0.02 Carbamazepine: 0.19 ± 0.01 Diclofenac: 0.15 ± 0.01 Progesterone: 0.13 ± 0.02 Medroxyprogesterone: 0.15 ± 0.02 Microcystin: 33.48 ± 16.20	
Temperature (°C)	22 ± 1	
PAC age (d)	0 10 60[a]	
PAC concentration (g dw/L)	1.1 ± 0.1	

[a]Kinetics also monitored on the corresponding abiotic control

2.3.3.2 Objective #4: "Evaluate the impact of the water temperature on the performance of the carbon contactor of an HMP" (Hypothese 5)

The Opaline B® pilot-plant was operated during the summer of 2011 and the winter of 2012. Operating the PAC contactor under contrasted temperature conditions produced aged PACs acclimated to these temperature conditions (Table 2-2). The acclimated PAC suspension was sampled and kept under the same temperature conditions to minimize the disturbance on the colonized PAC. DOC, RDOC, BDOC and ammonia removal kinetics monitored on 0-d, 10-d and 60-d PAC at 7±1°C and 22±1°C therefore reflect the impact of water temperature on the efficiency of DOC and ammonia removal in an HMP.

2.3.3.3 Objective #5: "Discriminate the relative importance of adsorption versus biological oxidation as mechanisms responsible for ammonia, DOC and micropollutants removal in the PAC contactor of an HMP" (Hypotheses 3, 4, 6)

The discrimination between the mechanisms occurring at the surface of the PAC was based on i) data from the removal kinetics at lab-scale and ii) the development of models discriminating the adsorbed fraction of a given contaminant removal from its oxidized fraction.

Removal kinetics

Discrimination of both mechanisms based on the experimental work included i) the comparison with kinetics conducted on an abiotic control for BDOC and micropollutants removal, ii) the production of nitrite and nitrate for ammonia removal and, iii) the sensitivity of the removal efficiency to water temperature for BDOC and ammonia removal. Since both the bacterial activity and adsorption onto PAC are potentially impacted by the water temperature, the sensitivity of the adsorption of the targeted compounds to the water temperature was investigated based on removal kinetics monitored on virgin PAC.

Ammonia. Nitrite and nitrate concentrations were measured along with the ammonia concentration during the removal kinetics assays at 7°C. These measurements allowed the determination of the fraction of ammonia removed by nitrification, while the difference was attributed to the adsorption of ammonia. As nitrite and nitrate measurements were only available under cold water conditions, the water temperature was used to discriminate ammonia adsorption from nitrification on colonized PAC. The sensitivity of ammonia adsorption to the water temperature was demonstrated as marginal on 0-d PAC. The fraction of ammonia adsorbed on PAC was therefore considered to be the same under both temperature conditions tested. The remaining removal percentage of ammonia at 22°C was attributed to nitrification.

DOC. Most of NOM removal studies focus on DOC removals. In this study, the RDOC and BDOC concentrations depletion was also monitored. RDOC is the refractory (non-biodegradable) fraction of the DOC. Its removal is therefore attributed to adsorption only. In contrast, the biodegradable fraction of DOC is potentially removed by adsorption and by biodegradation. Monitoring DOC, BDOC and RDOC therefore provides useful information for the discrimination of adsorption and biodegradation. Abiotic controls were also produced for 10-d and 60-d PAC based on the gamma-irradiation method optimized in Chapter 4. DOC, BDOC and RDOC

removal kinetics were conducted under the exact same conditions on colonized PAC and their abiotic control. BDOC removals obtained on the colonized PACs and their respective abiotic controls were compared by a repeated measures analysis of variance in the software Statistica 12 (Statsoft, USA). The fraction of BDOC removed by the irradiated PAC corresponds to the adsorbed fraction of BDOC, while the difference between BDOC removal on the PAC and its corresponding abiotic control corresponds to the biodegraded fraction of the total BDOC removal. As the irradiated PAC was only available under cold water conditions, the water temperature was used to discriminate BDOC adsorption from biodegradation on colonized PAC. As RDOC and BDOC adsorption percentages were demonstrated to be the same on 0-d PAC, the difference between total BDOC removal percentage and the percentage due to adsorption (identical to the RDOC percentage) was attributed to biodegradation at 22°C.

Micropollutants. Micropollutants adsorption kinetics at 22°C on 60-d PAC and its corresponding abiotic control produced based on the optimized method developed in Chapter 4 were compared. As micropollutants kinetics were not modeled during this research project, the contact time required to reach a 99% of each micropollutant removal were compared using a paired t-test in Excel (Microsoft Office 2007).

Modeling of ammonia and DOC removal

Two models both accounting for adsorption and biodegradation/nitrification were developed based on the kinetics monitored at lab-scale. These models describe the performance of the PAC contactor of the HMP under the operating conditions tested. The adsorbed and oxidized fractions were predicted by distinctive terms in the equations. Therefore, the models developed in this research project predict the fractions of DOC and ammonia removed by adsorption and by the bacterial activity in the PAC contactor of an HMP under the operating conditions tested.

The modeling approach is detailed in Chapter 4, Chapter 5 and Chapter 6. In short, the biological oxidation was described using the classical Monod type equation after which an Arrhenius law was used to represent the dependence of the biological activity to the water temperature. The first modeling approach to describe the adsorption kinetics was using a pseudo-second order (PSO) model, as they are largely applied in liquid-phase systems (Wu et al., 2009). Modeling the adsorption kinetics of ammonia and RDOC with PSO kinetics was used to compare adsorption capacities and adsorption kinetics rates on different PACs (i.e. PACs varying in age or pre-

exposed to gamma-irradiation) in Chapter 4 and Chapter 5. Another approach was proposed in Chapter 6 to describe the performance of the PAC contactor of an HMP for DOC adsorption. In this alternative modeling design, the PAC contactor was considered to follow an exhaustion curve such as the ones observed in biological filters. The description of the dependence of DOC adsorption to PAC aging was based on empirical observations at the pilot scale. As the PAC age was maintained stable in the pilot plants by daily purges and renewal of a fraction of the PAC, it was decided to integrate the PAC distribution of the aged PAC samples in the modeling approach. The PAC age distributions of both 10-d and 60-d PACs were estimated using Excel (Microsoft Office 2007). The PAC age distribution was calculated assuming perfect mixing and a daily renewal of 10% (10-d age distribution) and 1.7% (60-d age distribution) of the mass of PAC in the carbon contactor. Therefore, not only did the model provide the DOC removal percentage attributed to adsorption, but integrating the PAC age distribution in the model provided further insight on describing which fraction of the PAC was actually responsible for the DOC adsorption.

2.3.3.4 Objective #6: "Differentiate the relative importance of the HRT, the PAC age and the PAC concentration as key operating parameters on the optimization of the performance of the PAC contactor of an HMP" (Hypotheses 3-7)

As presented in Table 2-2, ammonia, DOC and micropollutants removals were monitored over increased contact times. Characterizing the removal kinetics allowed to determine the importance of the contact time on the removal of each of the dissolved compounds under the investigated conditions. Ammonia, DOC and micropollutants removal kinetics were also monitored at several PAC concentrations and PAC ages (Table 2-2). Repeated measures analysis of variance in the software Statistica 12 (Statsoft, USA) determined the statistical significance of the differences in efficiency obtained under the wide range of operating conditions tested. Finally, the comparison of the values obtained for the parameters of the developed models provided additional information on the relative importance of the contact time, the PAC concentration, and the PAC age for the efficiency of the process.

Table 2-3 presents the specific methodology developed to validate or invalidate the research hypotheses of this project.

Table 2-3: Experimental approach developed to validate (or invalidate) the research hypotheses

	Hypothesis	Scale	Experimental approach	Expected results
1	Active heterotrophic and nitrifying bacteria colonize the PAC in the contactor of an HMP operated at steady-state with mean PAC ages of 10 days and 60 days	Laboratory	Adaptation of methods developed for colonized GAC to PAC: heterotrophic plate counts (HPC), bacterial ATP, EPS: proteins and polysaccharides, ^{14}C-glucose respiration rate (PGR), oxidized nitrogen production (PNA) Development of a new method based on acetate consumption rates (PAU)	Comparison of various methods successfully adapted to colonized PAC and original method developed to evaluate the active heterotrophic biomass on the surface of colonized PAC based on the acetate consumption rate Quantification of the active heterotrophic and nitrifying biomass developed on 10-d and 60-d PAC
2	It is possible to define an optimized dose of gamma-rays that inhibits the active biomass of a colonized PAC without significantly altering its adsorptive properties	Laboratory &Modeling	HPC measurements and methylene blue (MB) adsorption kinetics on irradiated and non-irradiated colonized PAC Minimal dosage of gamma-rays based on HPC measurements and maximal dosage of gamma-rays based on PSO parameters for MB adsorption Comparison of RDOC adsorption PSO parameters and comparison of the active biomass (PGR and PAU) on colonized PAC and on irradiated colonized PAC at the optimized dosage	Gamma-irradiation is a suitable method to produce an abiotic control for colonized PAC Protocol for determining the optimal dose of gamma-rays to apply to produce an abiotic control Production of abiotic controls of 10-d and 60-d PAC

Table 2-3: Experimental approach developed to validate (or invalidate) the research hypotheses (continue).

	Hypothesis	Scale	Experimental approach	Expected results
3	Ammonia removal on colonized PAC is due to the nitrifying activity of the autotrophic biomass. Ammonia adsorption on colonized PAC is negligible	Laboratory &Modeling	Monitoring of ammonia removal kinetics on 0-d, 10-d and 60-d PAC for 60 minutes Assays conducted at 7°C and 22°C Nitrite and nitrate production monitored during ammonia removal kinetics to determine the fraction of ammonia nitrified Modeling of the adsorbed and oxidized fractions of ammonia	Discrimination between adsorption and nitrification as mechanisms responsible for ammonia removal Characterization of ammonia removal kinetics in a PAC contactor of an HMP
4	DOC removal in the PAC contactor of an HMP is due to a combination of its adsorption onto PAC and its biodegradation by the heterotrophic biomass developed on the PAC	Laboratory &Modeling	Monitoring of RDOC, BDOC and DOC removal kinetics on 0-d, 10-d, 60-d PAC and abiotic controls for 60 minutes. Assays conducted at 7°C and 22°C Modeling of the adsorbed and oxidized fractions of DOC	Discrimination between adsorption and biodegradation as mechanisms responsible for DOC removal based on removal kinetics and a model predicting DOC removal by a suspension of aged PAC in an HMP Characterization of DOC, BDOC and RDOC removal kinetics in a PAC contactor of an HMP
5	Natural organic matter biodegradation and nitrification kinetics on colonized PAC follow a Michaelis-Menten law, of which the parameters are affected by the water composition and temperature	Laboratory &Modeling	Monitoring of BDOC biodegradation and nitrification kinetics on 10-d and 60-d PAC in various water matrices Assays conducted at 7°C and 22°C Modeling of BDOC biodegradation and nitrification kinetics	Model predicting ammonia nitrification by 10-d and 60-d PAC in the PAC contactor of an HMP Model predicting BDOC biodegradation by 10-d and 60-d PAC in the PAC contactor of an HMP Value of the Michaelis-Menten parameters for BDOC and ammonia oxidation in warm and cold water under various water matrices

Table 2-3: Experimental approach developed to validate (or invalidate) the research hypotheses (continue).

	Hypothesis	Scale	Experimental approach	Expected results
6	A residual adsorption capacity on10-d and 60-d PAC is responsible for significant micropollutants removal in an HMP	Laboratory	Spike of a mixture of micropollutants in the water matrix Monitoring of micropollutants removal kinetics on 0-d, 10-d and 60-d PAC and irradiated 60-d PAC	Demonstration of the potential of the HMP using aged PAC to face a peak concentration of micropollutants
7	The PAC age, the PAC concentration and the HRT are operating parameters to consider for the optimized operation of the HMP	Laboratory &Modeling	Dissolved compounds removal kinetics monitored over a wide range of operating conditions Model predicting DOC and ammonia removal under the operating conditions tested	Relative importance of HRT, PAC age and PAC concentration for the removal of ammonia, DOC and micropollutants in the PAC contactor of an HMP Recommendations for the optimization of the process

CHAPTER 3 ARTICLE 2 - QUANTIFYING BACTERIAL BIOMASS FIXED ONTO BIOLOGICAL ACTIVATED CARBON (PAC AND GAC) USED IN DRINKING WATER TREATMENT

Quantifying methods developed for biological GAC were adapted to PAC. In parallel, a method based on the evaluation of the potential acetate uptake (PAU) rate was developed to quantify the active heterotrophic biomass on colonized PAC. This chapter presents estimations of the heterotrophic bacterial biomass onto colonized activated carbon by six different methods. It also compares the results obtained with the six methods under investigation on several colonized PACs and a colonized GAC. Results demonstrate that the biomass on aged PAC is comparable to the biomass on GAC from biological filters. The PAU method was demonstrated as a good alternative to PGR rate measurements. This chapter is a paper published in the *Journal of Water Supply: Research and Technology – AQUA*.

QUANTIFYING BACTERIAL BIOMASS FIXED ONTO BIOLOGICAL ACTIVATED CARBON (PAC AND GAC) USED IN DRINKING WATER TREATMENT

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ABSTRACT

Hybrid processes coupling the use of powder activated carbon (PAC) with membrane filtration for drinking water production are emerging as promising alternatives to conventional technologies due to their enhanced control of dissolved contaminants. The quantification of biomass colonizing PAC is crucial for modeling, designing control strategies and improving the overall performance of these processes. The aim of this study was to examine the applicability of several common methods developed for colonized granular activated carbon (GAC) to PAC. Six analytical methods (based on the measurement of proteins, polysaccharides, heterotrophic plate counts, potential glucose respiration, bacterial ATP and a potential acetate uptake rate, which is proposed herein) were compared. The results showed that the rates of glucose respiration and of acetate consumption could be used interchangeably. Proteins were also an interesting alternative for on-site measurements. It was concluded that biological PAC-based processes sustained a level of heterotrophic activity similar to or greater than that observed in GAC biofilters.

KEYWORDS

Biofilters - drinking water - extracellular polymeric substances - microbial activity - substrate uptake rates

3.1 Introduction

Biological filters have been used extensively for the production of drinking water in North America and Europe. Some of their advantages include the biological stabilization of treated water via the removal of dissolved organic matter and ammonia, a decrease in chlorine demand and the formation of fewer disinfection by-products. Currently, these processes are becoming increasingly important due to the rise of green technologies and the emergence of new contaminants that may be amenable to biodegradation, such as several pharmaceuticals, taste and odor compounds and cyanotoxins (Brown, 2007). Granular activated carbon (GAC) is the preferred medium for biological filters because it offers more sites for microbial attachment than non-adsorptive supports (e.g., sand or anthracite) (Wang et al., 1995). Moreover, both the irregular surface and the porous structure of GAC protect the biomass against shear forces and toxic loads (Chaudhary et al., 2003; Herzberg et al., 2003).

Recent developments in membrane technologies for drinking water production include the integration of powder activated carbon (PAC) in processes referred to as hybrid membrane processes (HMPs) (Stoquart et al., 2012). PAC targets dissolved compounds that are not retained by low-pressure membranes. It offers faster adsorption rates than GAC (Yener et al., 2008) and can be injected and recovered continuously from a slurry-type suspension. This configuration offers high flexibility to address sudden source water quality variations by simply adjusting the age of the PAC slurry to control adsorption performance (Stoquart et al., 2012).

When using activated carbon (AC), biodegradable compounds can be removed by adsorption, biodegradation or a combination thereof. Within the HMP, the relative importance of both mechanisms is intimately related to the age of the PAC slurry. Assessing the relative importance of both mechanisms is paramount for modeling the process and thus optimizing its performance. Therefore, reliable techniques for evaluating microbial colonization onto PAC are required.

Several methods have been developed to evaluate bacterial biomass fixed on GAC. As proposed by Lazarova et al. (1994), they can be classified as either non-destructive or destructive (i.e., techniques that disrupt the biofilm). Non-destructive methods include direct microscopy and techniques based on the measurement of specific activities, such as the potential glucose respiration (PGR) (Servais et al., 1991), the overall oxygen consumption (Urfer et al., 2001) or the potential nitrifying activity developed to estimate the autotrophic nitrifying biomass (Kihn et al., 2000). On the other hand, destructive methods, which require detaching the biomass from the support media, include total cell counting by epifluorescence (Nishijima et al., 1997), the enumeration of heterotrophic plate counts (HPC) (Camper et al., 1985a, 1985b) and the measurement of compounds related to the viable biomass, such as phospholipids (Wang et al., 1995) and ATP (Velten et al., 2011), and the biofilm density, such as the concentrations of polysaccharides (Quintelas et al., 2008) and proteins (Drogui et al., 2011; Papineau et al., 2013) in extracted extracellular polymeric substances (EPS).

All the aforementioned techniques have only been applied to GAC, not biological PAC. Non-destructive methods are the most interesting because the detachment of the biomass is undesirable due to issues such as incomplete recovery and the impact of the procedure on cellular integrity (Lazarova et al., 1994). Amongst the non-destructive methods, PGR allows the biomass potentially responsible for the removal of biodegradable compounds to be evaluated. However,

the PGR method requires the use of a radiolabeled substrate (i.e., ^{14}C-glucose), which is expensive, not always readily available and may pose logistical challenges. One promising alternative substrate is acetate, a ubiquitous compound that can be used as a substrate by almost all eubacterial and fungal cells (Wang et al., 1995). For instance, the abundance of acetate-utilizing bacteria has been estimated microautoradiographically as 47-93% of the total bacteria in wastewater-activated sludge (Nielsen et al., 2002). In addition, acetate is a common ozonation by-product (Urfer et al., 2001). Hence, acetate-biodegraders are likely to be present in drinking water biofilters. Moreover, acetate is poorly adsorbable onto GAC (Moteleb et al., 2002) and PAC (Stoquart et al., 2013), which minimizes potential bias in the evaluation of the acetate uptake rate. Thus, measuring the potential acetate uptake (PAU) rate could be an interesting alternative for evaluating active bacterial biomass fixed on solid media.

To the best of our knowledge, no published studies have aimed to quantify the biomass developed on the PAC surface from drinking water treatment processes. This work was thus conducted to evaluate the applicability of several existing analytical methods (i.e., the assessment of PGR, HPC, ATP and EPS) and to propose a new method based on measuring PAU rates for characterizing heterotrophic biomass on biological PAC obtained from two hybrid pilot membrane processes. The results obtained for PAC were also compared with those measured on a biological GAC (BAC) sample collected from a full-scale biofilter. Finally, the results obtained from the six tested analytical methods were compared.

3.2 Materials and Methods

3.2.1 Description of samples

3.2.1.1 AC characteristics

Three types of wood-derived AC commercialized by Pica™ (Picahydro LP 39, Picahydro L30-260 and Picabiol 2) were tested; the non-colonized media are referred to as NP25, NP200 and NGAC, respectively. NP25 and NP200 are PAC with median particle sizes of 15-35 µm and 210-260 µm, respectively. NGAC has a median particle size of 500-700 µm. Their iodine numbers vary between 900 and 1000 mg/g.

3.2.1.2 AC colonization

The colonization of PAC was carried out in four parallel HMP pilots operating under two configurations. The pilots were fed with coagulated-settled river water (Des Mille-Iles River, Laval, Canada). The average main influent characteristics were 2.9 mg DOC/L, 0.23 mg BDOC/L and 154 µg N-NH_3/L. In the first configuration (PAC/UF), the PAC treatment was integrated to a submerged ultrafiltration (UF) unit described in detail by Léveillé et al. (2013). Two PAC/UF reactors were filled with NP25. In the first AC/UF reactor (P7-5), a PAC concentration of 5 g dry weight (dw)/L, a solids retention time (SRT) of 7 days and a hydraulic residence time (HRT) of 69 min were maintained. In the second PAC/UF pilot (P60-10), the PAC concentration, the SRT and the HRT were 10 g dw/L, 60 days and 77 min, respectively.

In the second configuration (PAC+UF), water was fed into two parallel stirred-tank reactors filled with NP200, which was maintained inside the reactors using a 55-85 µm sieve. The effluent water was then fed into the UF modules. The PAC concentrations within the reactors were 1 g dw/L (P67-1) and 5 g dw/L (P67-5). Unlike the PAC/UF configuration, both reactors were operated continuously without any PAC replacement (i.e., with variable SRT). At the sampling time, an SRT of 67 days had been reached in both PAC+UF reactors.

The BAC samples were obtained from the surface of a full-scale dual media filter (80 m^2 surface area) composed of layers of sand (D_{10} = 0.45 mm, H =15 cm) and GAC (with NGAC-type characteristics; H = 180 cm). The empty bed contact time (EBCT) in the filter ranged from 20-30 min depending on the water demand.

A summary of the characteristics of the five colonized AC samples is presented in Table 3-1.

Table 3-1 : Biological AC sample characteristics

Sample ID[a]	Type of carbon	Median diameter (µm)	Pilot unit	Carbon used for starting up the pilot	SRT (days)	Concentration in the reactor (g dw/L)
P7-5	PAC	15-35	PAC/UF[b]	NP25	7	5
P60-10	PAC	15-35	PAC/UF[b]	NP25	60	10
P67-1	PAC	210-260	PAC+UF[c]	NP200	67	1
P67-5	PAC	210-260	PAC+UF[c]	NP200	67	5
BAC	GAC	500-700	Biological GAC	NGAC	N.A.[d]	350

[a] The first number refers to the age (d) of the carbon and the second number refers to the PAC concentration (g dw/L) within the contactor
[b] Hybrid membrane process with integrated activated carbon treatment
[c] Hybrid membrane process with activated carbon pretreatment
[d] N.A.: not available

3.2.2 Biomass measurements

The biomass measurements were performed on the same day for all analytical techniques and sample types tested (i.e., the five colonized samples and the three virgin samples). The virgin samples (NP25, NP200 and NGAC) were used as controls. Before any experiment, 10 g dw of each of the virgin AC samples was humidified overnight at room temperature in 1 L of Milli-Q water. The pH of the slurry (approximately 3) was raised to 7.0 by adding 1 M NaOH. The colonized PAC slurries (P7-5, P60-10, P67-1 and P67-5) were withdrawn at the same time from the four reactors. All the PAC samples (colonized and virgin) were recovered by filtration on a Grade 41 paper filter (Whatman). Finally, the BAC sample was collected from the surface of the biofilter.

3.2.2.1 PAU rate

According to Monod kinetics, the rate of substrate depletion (*dS/dt*) and the specific microbial growth rate (μ) can be expressed by Eq. 3-1 and Eq. 3-2, respectively.

$$\frac{dS}{dt} = -\frac{\mu X}{Y} \qquad \text{Eq. 3-1}$$

$$\mu = \mu_{max} \frac{S}{S + K_S} \quad \text{Eq. 3-2}$$

where X is the biomass concentration, Y is the growth yield, μ_{max} is the maximum specific growth rate and K_s is the half-saturation constant. Eq. 3-3 is obtained by substituting Eq. 3-2 into Eq. 3-1 as follows:

$$\frac{dS}{dt} = -\frac{\mu_{max} X}{Y} \cdot \frac{S}{S + K_S} \quad \text{Eq. 3-3}$$

If $S >> Ks$, Eq. 3-3 can be simplified as

$$\frac{dS}{dt} = -\frac{\mu_{max} X}{Y} \quad \text{Eq. 3-4}$$

q_S, the specific substrate removal rate, is defined by Eq. 3-5.

$$q_S = -\frac{dS}{X\, dt} \quad \text{Eq. 3-5}$$

Thus, Eq. 3-4 can be rewritten to give Eq. 3-6.

$$q_S = \frac{\mu_{max}}{Y} \quad \text{Eq. 3-6}$$

Eq. 3-6 shows that under substrate saturating conditions (i.e., $S >> Ks$), the substrate is removed following zero-order kinetics during the first few hours of incubation. Thus, q_S (hereafter referred to as the PAU rate) can be considered an estimate of the microbial biomass fixed on the media because the uptake rate and biomass are proportional (Eq. 3-6).

The PAU rates were estimated in 1 L beakers containing 500 mL of test medium. The latter contained a saturating initial concentration of sodium acetate (15 mg Na-acetate/L, equivalent to 4.4 mg C/L) and was supplemented with NH_4Cl (0.65 mg N/L) and phosphate buffer (0.06 mg P/L). After adding 10 g wet weight (ww) of activated carbon, the slurries were maintained at 20°C under agitation at approximately 150 rpm using a magnetic stirrer. Samples were withdrawn periodically by filtering 40 mL of slurry through a 0.45 µm polyethersulfone membrane previously rinsed with 1 L of Milli-Q water.

The acetate concentration was determined in duplicate samples by ion chromatography (Dionex Corporation, Sunnyvale, U.S.A.). The apparatus was equipped with an IonPac AS18 column and suppressed conductivity detection. An EluGen® EGC-KOH cartridge was used as the eluent. The limit of detection, the limit of quantification, the reproducibility and the accuracy of this method are 0.0159 mg/L, 0.0530 mg/L, 3% and 4.5%, respectively. The PAU rates were calculated from the initial slope of the acetate content obtained by linear regression, normalized per gram of AC dw in the assay. These rates are expressed as specific acetate uptake rates in mmol Na-acetate per g AC dw per hour. Regressions made to calculate PAU rates were always significant ($p < 0.05$) with $R^2 > 0.96$, excepting for P7-5 ($R^2 = 0.61$) and P60-10 ($R^2 = 0.72$).

3.2.2.2 PGR rate

The production of $^{14}CO_2$ due to the mineralization of ^{14}C-glucose under saturating conditions was measured according to the method of Servais et al. (1991). This method uses a similar fundamental approach to the PAU method, although radioactive glucose replaces acetate as a substrate and mineralization (CO_2 production) is measured rather than substrate consumption. A mixture containing ^{14}C-glucose and non-radiolabeled glucose was prepared to obtain a final glucose concentration of 1 mM and a radioactivity of 0.1-1 µCi/mL. One milliliter of this mixture was added to 1 g ww of AC in a penicillin flask closed with a rubber septum. After 3 h of incubation at 20°C, the sample was acidified by adding 2 mL of 10% H_2SO_4 through the septum. Samples were bubbled for 10 min to extract the CO_2, which was trapped in a mixture of Carbo-SorbE (Perkin Elmer) and PermafluorE+ (Perkin Elmer, 1:4 v/v). The radioactivity was determined by liquid scintillation with a Packard Tri-Carb (TR-1600) scintillation counter. The amount of glucose mineralized was measured in triplicate and expressed as nmol glucose per g AC dw per hour.

3.2.2.3 HPC

For each sample, 1 g ww of the AC sample was homogenized in a blender at 16,000 rpm and 4°C for 3 min with a mixture of Zwittergent (10^{-6} M), EGTA (ethylene glycol-bis-(β-aminoethyl ether)-N,N,N',N'-tetraacetic acid, 10^{-3} M), tris buffer (0.01 M, pH 7.0) and 0.1% peptone (Camper et al., 1985a). The culturable cells were analyzed in duplicate on decimal dilutions using the membrane filtration technique (9215 D Standard Methods,(American Public Health

Association (APHA) et al., 2012)). The membrane filters were incubated on R2A agar at 20°C in the dark. After seven days, the HPCs were determined and expressed in CFU per g AC dw.

3.2.2.4 Bacterial ATP

An ATP detection kit was used (Profile®-1 Reagent Kit, New Horizons Diagnostics, U.S.A). The kit consisted of a microluminometer, filtration devices (0.4 µm pore diameter), a lysing reagent for non-bacterial ATP (somatic releasing agent, SRA) and a second reagent ensuring both bacterial lysis and leaching of bacterial ATP (bacterial releasing agent, BRA). Prior to the analysis, the samples were homogenized, just as for the measurement of HPC, and then 10-fold diluted in phosphate buffer to minimize ATP adsorption on activated carbon. After the filtration of 225 µL of the suspension in the filtration device, 60 µL of SRA was added and evacuated twice to discard the non-bacterial ATP. In a second step, 60 µL of BRA was added to the sample in the Filtravette device, filtered and recovered. Finally, 25 µL of the filtrate was mixed with 225 µL of reconstituted luciferin-luciferase reagent (Molecular Probes®, U.S.A.) in a new Filtravette device and the relative luminescence units were recorded. Positive controls were obtained by adding two standards with high concentrations of ATP (ranging from 0.8 to 2.7 µg ATP/L) to the samples. The results were compared to a standard curve (0.01-3 ng ATP/L) and expressed as ng ATP per g AC dw. No replicates were made.

3.2.2.5 EPS: polysaccharides and proteins

EPS were extracted in duplicate using approximately 2 g ww of sample according to the method proposed by Liu et al. (2002). The samples were resuspended in 10 mL of phosphate buffer supplemented with 60 µL of formaldehyde (36.5% v/v) and then incubated at 4°C for one hour under agitation. After the addition of 4 mL of 1 M NaOH, the samples were incubated for three hours at 4°C. Next, the slurries were centrifuged twice at 12,000 *g* and 4°C for 15 min. Finally, the supernatants were recovered and filtered through sterile 0.45 µm pore size membranes.

The protein content of the extracts was determined using a bicinchoninic acid method-based commercial kit (Pierce© BCA Protein Assay Kit, Thermoscientific, U.S.A.) with a bovine serum albumin (BSA) standard. The results were expressed in mg of proteins (equivalent BSA) per g of AC dw or in mg C per g of AC dw, knowing that carbon represents 45% of the mass of BSA. The polysaccharides were analyzed by the phenol-sulfuric acid method using glucose as a standard

(Dubois et al., 1956). The results were expressed in mg polysaccharides (equivalent glucose) per g of AC dw or mg C per g of AC dw, knowing that carbon represents 40% of the molecular weight of glucose. The total amount of EPS was obtained by summing the concentrations of proteins and polysaccharides (both expressed as mg C per g of AC dw).

3.2.3 Dry weight

The virgin and biological AC were dried for 24 h at 105°C according to the standard method 2540 B (American Public Health Association (APHA) et al., 2012) to obtain the dry weights of samples. The results of all microbiological measurements were then expressed per g of AC dw.

3.3 Results and Discussion

The analytical methods described previously were applied to quantify the biomass fixed onto AC samples. Concerning biological PAC samples, different levels of biomass density were expected because the colonization was carried out under variable PAC ages and concentrations within the reactors. First, P7-5 and P67-5 were two PAC samples colonized at the same concentration in the pilot reactor (i.e., 5 g dw/L). Although these two PAC had distinctive sizes, no significant differences with respect to biomass density were expected due to this factor (Markarian et al., 2010). However, higher ages (67 vs. 7 days) were expected to lead to higher biomass densities for AC colonized under equivalent conditions. Second, two reactors were operated with the same PAC age (67 days) but variable PAC concentrations inside the reactor (P67-1 and P67-5). In that case, equivalent colonization (expressed per g of AC dw) is not expected; Markarian and collaborators (2010) noted that the development of biomass on biological PAC is limited by substrate availability rather than the available colonization surface. Consequently, it was hypothesized that PAC colonized at a lower concentration in the pilot reactor would support a higher biomass density on its surface. The results gathered from each analytical method are presented and discussed separately as follows.

3.3.1 PAU rates

No decrease in the acetate concentration was observed in the experiments conducted with virgin materials, even after 24 h of contact (data no shown). This finding confirms that any acetate removal is due to biological activity.

The initial acetate concentration applied in the assays was approximately threefold higher than K_s (the value embedded in Biowin™ software is 5 mg/L). This concentration led to the expected zero-order kinetics for acetate removal when the biomass growth is negligible compared to the biomass initially present on the AC. Hence, all colonized samples removed acetate at a constant rate during the first 4-6 h (Figure 3-1).

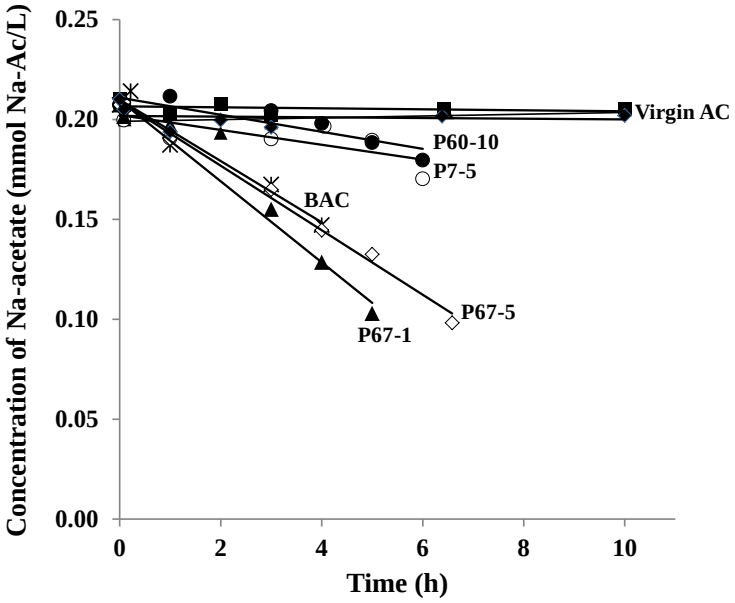

Figure 3-1 : Acetate uptake by virgin and colonized samples of activated carbon (AC). The symbols represent the experimental results, and the lines represent the data from the linear regression.

Figure 3-2a) depicts the results of the PAU tests. The lowest PAU rate was found for the P7-5 sample, which was expected to have the lowest level of bacterial colonization due to the short SRT of the reactor (7 days), whilst the maximum PAU rate was measured for the P67-1 sample (colonized at the highest SRT). Actually, the PAU rate measured for the P67-1 sample was not significantly different from that measured for the biological GAC filter (i.e., the BAC sample). Sample P67-5 presented a statistically significantly higher PAU rate than sample P7-5 ($p < 0.05$) confirming that higher SRT led to a higher active biomass on the PAC surface. In addition, the PAC samples colonized at a lower PAC concentration (P67-1) had a statistically significantly higher PAU rate than its counterpart colonized at 5 g/L (P67-5) ($p < 0.05$). In this way, the positive effect of a high substrate availability on the activity of the biomass fixed onto PAC appears to be confirmed too.

Based on these preliminary results, the measurement of PAU rates is a promising method. This finding should be confirmed by validating this method with a wider set of samples, including more BAC samples. In addition, monitoring the depletion of acetate in the first hours of the assay in short time intervals is necessary for properly monitoring the zero-order kinetics.

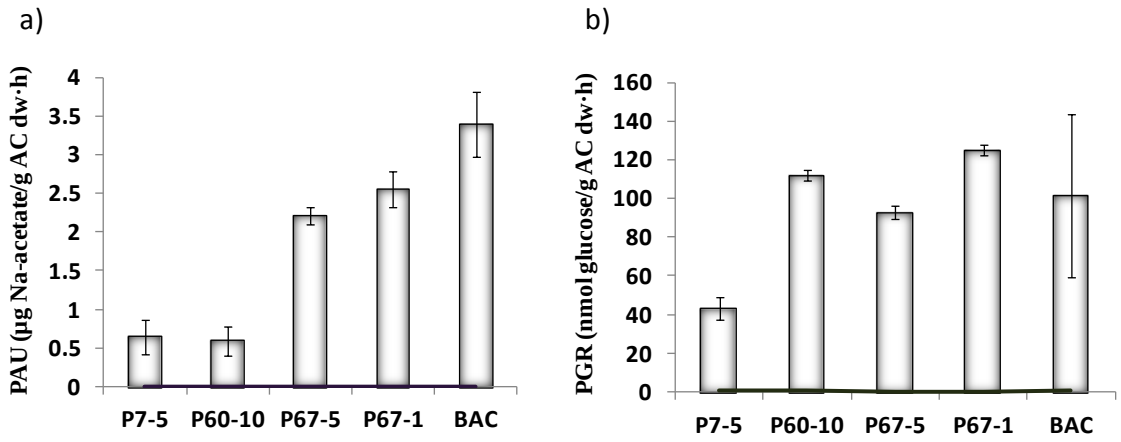

Figure 3-2 : (a) Potential acetate uptake (PAU) rates of biological AC samples. Error bars represent the standard errors of the regression slopes used for calculating PAU rates. (b) Potential glucose respiration rates of biological AC samples. Error bars represent standard deviations. Solid lines (—) represent the background values measured on the corresponding virgin samples.

3.3.2 PGR rates

Figure 3-2b) presents the PGR rates measured on colonized AC. The background values obtained for the virgin PAC were between 0.07 and 0.44 nmol/g AC dw·h. These values were not significantly different from one another ($p > 0.05$) and were considerably lower (120- to 1900-fold) than the values obtained for the colonized materials. Therefore, the PGR values shown in Figure 3-2b) and elsewhere in this paper were not corrected for the background measurement.

The PGR of the sample P7-5 (43.1 nmol/g AC dw·h) was significantly different from the virgin samples ($p < 0.05$). The PGR rates obtained for the samples with higher SRT (i.e., at least 60 days) led to the same conclusions as for the PAU method, with P60-10 being more colonized than P7-5 and P67-1 being more colonized than P67-5. All the samples with a high SRT presented a PGR not significantly different from the BAC sample.

To compare our results with the values of PGR found in the literature (usually reported as µg of C-biomass/cm^3), the PGR rates were converted by considering a mean density value of 1.33 g of

wet activated carbon per cm^3 and a correspondence factor of 1.1 µg C of bacterial biomass per nmol of glucose respired per hour. This last value was originally obtained by calibrating the radiochemical method with bacteria washed off from GAC filter samples and enumerated by epifluorescence microscopy (Servais et al., 1991). Following this conversion, our PGR values obtained for the colonized PAC samples ranged from 17.7 to 69.4 µg C/cm^3, whereas a biomass of 38.6 µg C/cm^3 was measured at the surface of the biological filter (sample BAC). This value is higher than the PGR measured previously by Niquette et al. (1998) at the top of the same full-scale GAC biofilter (20 µg C/cm^3). This difference could be partly explained by the temperature in the filter (16°C in our case vs. 11°C measured previously). In an another study reporting the colonization of a biofilter at 16°C, the PGRs were comprised between 2.5-10.9 µg C/cm^3 (Servais et al., 1991), while an average value of 4.7 µg C/cm^3 was proposed as representative of the fixed biomass in a GAC biofilter at steady state (Servais et al., 1991). The higher biomass densities observed on our PAC samples are most likely explained by the amount of support area available for the colonization and the nutrients limitation. Indeed, the PAC samples were colonized at low concentrations (i.e., 1 to 10 g/L), whereas a larger mass of GAC typically provides support for the colonization at the surface of a BAC filter. In addition, the biomass densities measured on BAC come from second-stage filters, while our PAC was colonized as a first-stage process. Niquette et al. (1998) observed a similar trend (i.e., higher colonization in first- as opposed to second-stage BAC filters). As described earlier, this result is explained by the higher nutrient loading offered in first-stage processes.

3.3.3 HPC

The results of the analysis of HPC are presented in Figure 3-3a). The densities of HPC on biological PAC ranged from $4.2 \cdot 10^7$ to $3.0 \cdot 10^8$ CFU/g PAC dw, whereas the value for the BAC sample was $3.3 \cdot 10^7$ CFU/g GAC dw. The results obtained are of the same order of magnitude as the literature values for BAC. However, no further comparison can be drawn. The culture conditions (i.e., culture medium and incubation temperature) applied were indeed highly variable, leading to potentially large variations in the HPC results. LeChevallier et al. (1984) measured 10^8 CFU/g GAC on a TLY medium, Camper et al. (1985b) measured $5 \cdot 10^7$ CFU/g GAC after incubating at 35°C, and Niemi et al. (2009) measured $6 \cdot 10^7$ to 10^8 CFU/g GAC dw after incubating at 25°C.

As mentioned before, the detachment of bacterial cells from the support medium is critical when using the plate count procedure to assess biomass density. In this study, the higher values of culturable cells obtained for biological PAC may be the result of the homogenization step being more efficient for smaller particles. Indeed, the shear stress is inversely proportional to the cross-sectional area of the material with area parallel to the applied force vector.

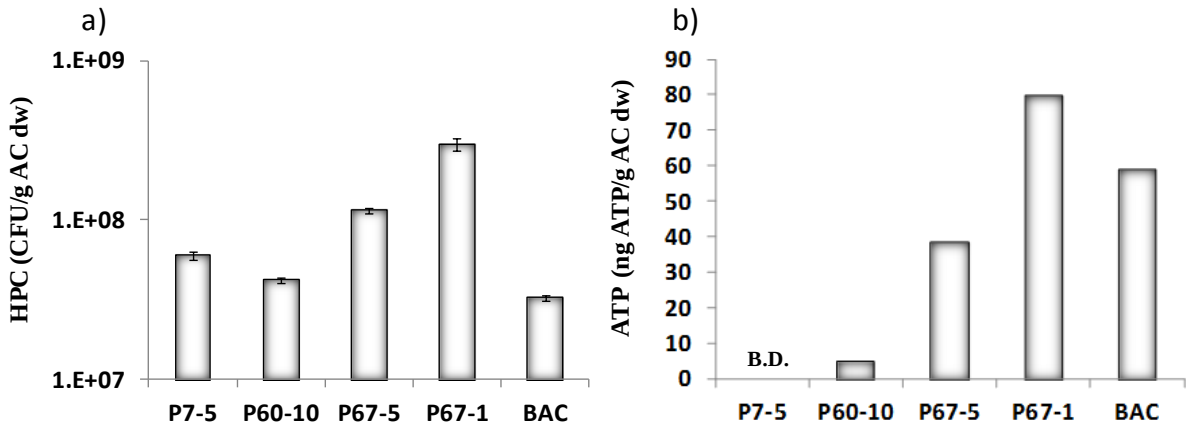

Figure 3-3 : (a) Heterotrophic plate counts in biological AC samples. Error bars represent standard deviations. (b) Bacterial ATP contents in biological AC samples. B.D.: Below detection limit.

3.3.4 Bacterial ATP

The results obtained for the bacterial ATP are presented in Figure 3-3b). The ATP concentration measured on sample P7-5 was below the detection limit, whereas sample P60-10 presented an ATP concentration of only 5 ng ATP/g PAC dw. Samples P67-5 and P67-1 presented ATP concentrations of 39 and 80 ng ATP/g PAC dw, respectively. These results may have been biased by the impact of residual adsorption. Positive controls confirmed that ATP readily adsorbed onto PAC particles. Luminescence losses ranging from 70 to 99% were detected after the addition of an ATP standard to the PAC. Thus, the residual adsorption capacity of PAC is an important concern when using ATP and future work should aim for an improved separation of the biofilm from the PAC particles before conducting the ATP analysis.

For colonized GAC, the measured value (58.9 ng ATP/g BAC dw or 14.07 ng ATP/g BAC ww) was lower than the usual ATP contents. Niemi et al. (2009) measured 0.5-0.7 nmol ATP/g GAC dw (equivalent to 254-355 ng/g GAC dw), while Velten et al. (2011) measured 1170 ng ATP/g

GAC ww at the surface of a fully colonized biofilter. In the former case (Niemi et al., 2009), a prior extraction of the ATP had been carried out, thereby indicating that the method used herein could most likely be improved by including an ATP extraction step before the addition of the luciferin-luciferase complex.

3.3.5 EPS: polysaccharides and proteins

The results of the analysis of extracellular proteins and polysaccharides are presented in Figure 3-4a). The proteins ranged from 6.7 to 14.0 mg/g PAC dw and 8.1 mg/g BAC dw (or 1.9 mg/g BAC ww). The results obtained for the BAC were lower than those obtained in laboratory-scale GAC columns removing microcystin-LR from drinking water (17.2-37.2 mg/g GAC ww) (Drogui et al., 2011). Polysaccharides were present at lower concentrations than proteins: 1.0 to 3.6 mg/g PAC dw and 5.1 mg/g BAC dw. Figure 3-4b) presents the total EPS measurements as well as the polysaccharide-to-protein ratio. The calculated polysaccharide-to-protein ratios were similar in the various samples of biological PAC with SRT of at least 67 days (0.22 ± 0.04). The youngest PAC (i.e., P7-5) had a lower ratio (0.13 ± 0.002), whereas the GAC sample cumulated the greatest amount of polysaccharides (0.56 ± 0.1). As a reference, higher polysaccharide-to-protein ratios have been associated with higher SRT in activated sludge (Massé et al., 2006; Satyawali et al., 2009), which is consistent with our results. In fact, the relative abundance of polysaccharides over proteins has been explained by the slower hydrolysis rate of polysaccharides (Massé et al., 2006). The increase in the polysaccharide-to-protein ratios at high SRT could also arise from a higher polysaccharide production, which would increase the bacterial adhesion to AC. Indeed, polysaccharides are widely recognized to as key in mediating both cell-to-cell interactions and cell attachment to supports (Tay et al., 2001). As polysaccharides tend to accumulate (cf. low hydrolysis rate), this technique may lead to an improper assessment of AC microbial colonization for high SRT. In particular, comparing fully colonized samples with different SRT is not possible because old AC should lead to higher polysaccharides contents for the same amount of active biomass. However, by considering the total amount of EPS (i.e., the sum of proteins and polysaccharides) as presented in Figure 3-4b), similar trends as the one observed for the potential activity-based methods (i.e., PAU and PGR) were obtained.

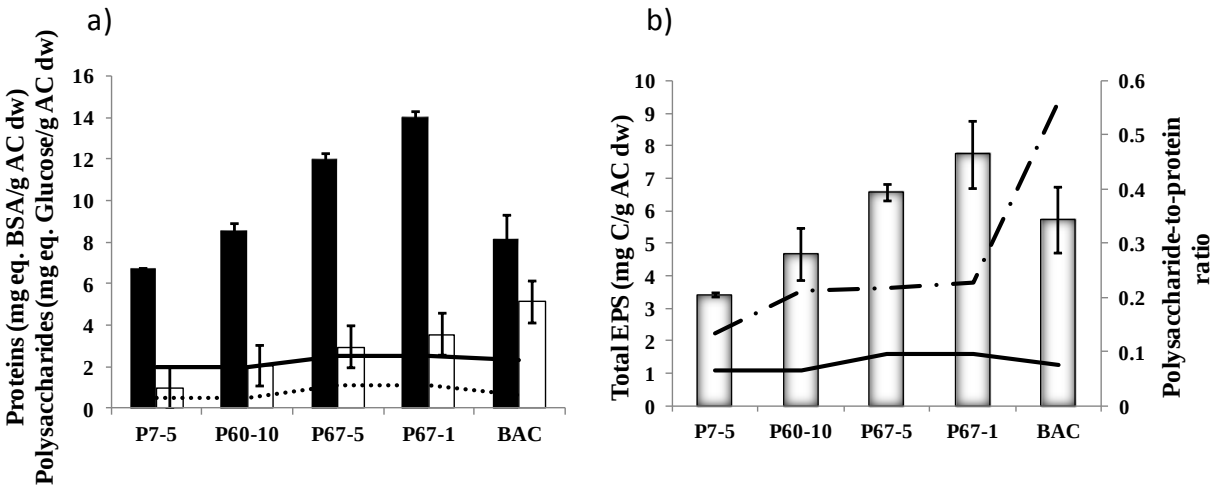

Figure 3-4 : (a) Measured (■) proteins, (——) background proteins, (□) polysaccharides and (·····) background polysaccharides in biological AC samples. (b) Measured (□) total EPS, (——) background total EPS and (– · –) polysaccharide-to-protein ratio in biological AC samples. Error bars represent standard deviations.

3.3.6 Comparison of methods

A comparison was performed by considering all the tested methods except for the ATP method, which remains to be optimized. Figure 3-5 compares the results obtained with our reference method (i.e., PGR) and the results of the PAU rates, log HPC and the contents of proteins, polysaccharides and total EPS. The corresponding correlation matrix is presented in Table 3-2. This matrix confirms that the results of the PAU tests were significantly correlated with the PGR values (r = 0.82), suggesting the possibility of using either technique interchangeably. In addition, there were strong correlations between methods based on potential activity and the EPS analysis (r > 0.75). The total EPS and proteins were better correlated with the PGR method (r = 0.92 and 0.89, respectively), whereas the polysaccharides results were better correlated with the PAU data (r = 0.96).

All of the methods investigated differentiated between the colonized AC and the corresponding virgin material ($p < 0.05$) for all of the samples tested. As confirmed by the background measurements, the EPS methods were the least sensitive (see background measurements on Figure 3-4a) and Figure 3-4b)). In contrast, the PGR method was the most sensitive method. Indeed, by raising the ratio of the radioactive specific activity of the glucose solution added to the

AC (by increasing the proportion of radioactive glucose in this solution), the sensitivity can be easily improved.

Among biological PAC samples, P67-1 carbon exhibited the maximum results of all the six analytical methods, which were higher than those presented by the P67-5 sample. The enhanced microbial colonization of P67-1 carbon might be due to the higher substrate availability that prevailed in this reactor (with the lowest PAC concentration). No statistically significant difference was found between the P67-1 and BAC samples using the PGR method ($p > 0.05$), although this finding may be attributed to the considerable standard deviation of the BAC results (i.e., 41%). The total EPS method indicated that the P67-1 sample was more colonized than the BAC sample, whereas the opposite was true for the PAU method. These results support the idea that the biomass of a PAC-based process is as active as the biomass at the surface of a conventional biological GAC filter for drinking water treatment.

Both potential activity-based methods (PGR and PAU) could be used to improve the modeling of DOC and BDOC removal as well as the control strategies and the overall performance of biological processes used in drinking water production. The protein measurements were highly correlated with the potential activity methods (see Table 3-2). From an operational viewpoint, the protein analysis is the least cumbersome and time-consuming of all techniques tested during this project. It could be used as an easily measurable surrogate for monitoring the microbial activity on biological AC in water treatment plants.

It is worth highlighting that, amongst the methods tested, the PAU and PGR rates and HPC methods were designed to provide data on the heterotrophic biomass while the ATP and the EPS measurements allowed the evaluation of not only the heterotrophic bacteria, but the entire bacterial and non-bacterial biomass. These differences should be kept in mind and the investigation of the microbial communities established at the surface of the AC under variable SRT would provide additional insight on the results of the different methods applied in this study.

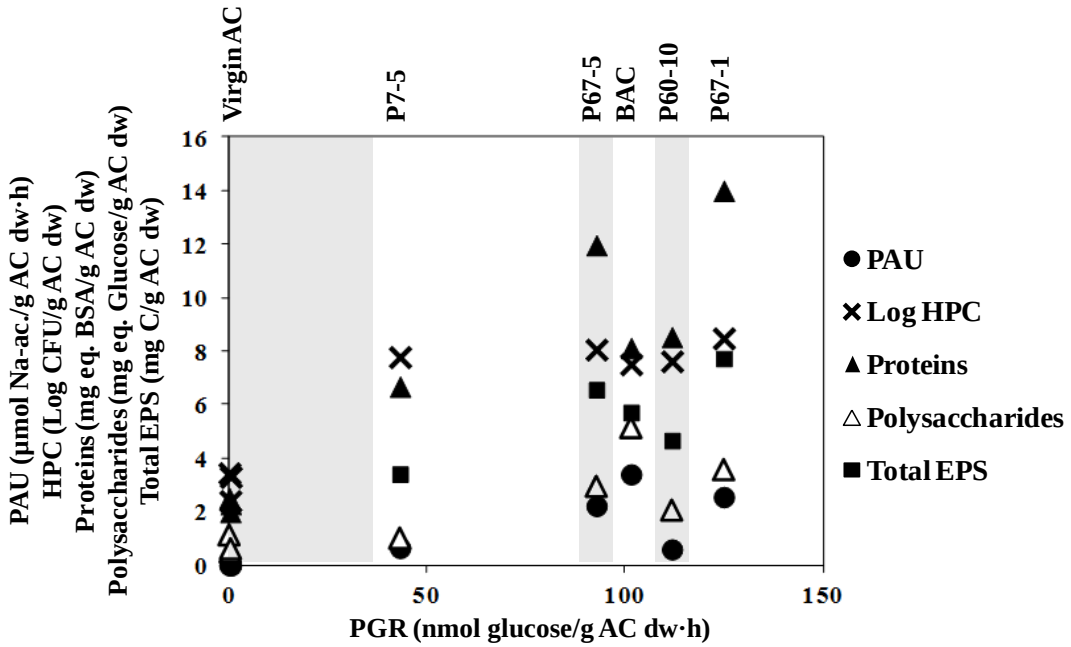

Figure 3-5 : PAU rate, Log HPC, proteins, polysaccharides and total EPS as a function of the PGR rate measured on biological and virgin AC samples.

Table 3-2 : Correlation matrix (r-values, $p < 0.05$) between the results obtained with the PAU, PGR, Log HPC, proteins, polysaccharides and total EPS methods.

	PAU	**PGR**	**Proteins**	**Polysac.**	**Total EPS**	**Log HPC**
PAU	1	0.82	0.80	0.96	0.88	0.72
PGR	0.82	1	0.89	0.84	0.92	0.87
Proteins	0.80	0.89	1	0.75	0.98	0.81
Polysac.	0.96	0.84	0.75	1	0.85	0.66
Total EPS	0.88	0.92	0.98	0.85	1	0.89
Log HPC	0.72	0.87	0.81	0.66	0.89	1

* Polysac.: Polysaccharides

3.4 Conclusions

The results from PAU, PGR, EPS and HPC methods were strongly correlated. The PAU rate is a promising method to assess the bacterial activity on PAC and GAC. However, it should be validated for a wider set of colonized AC samples. Because protein content is well correlated with the PAU and PGR results, it would be a good surrogate for on-site biomass measurements. A high SRT increased the activity of heterotrophic biomass and the amount of EPS associated to the biofilms. Finally, it was concluded that heterotrophic activities comparable to BAC filters can be obtained in biological PAC-based drinking water systems.

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CHAPTER 4 ARTICLE 3 - GAMMA IRRADIATION: A METHOD TO PRODUCE AN ABIOTIC CONTROL FOR BIOLOGICAL ACTIVATED CARBON

As the presence of a significant active biomass was demonstrated on aged PAC (Chapter 3), an abiotic control of the colonized PAC was required to properly discriminate the adsorption from the biological oxidation of the compounds removed by aged PAC suspensions in HMPs. In this chapter, gamma-irradiation is demonstrated as a suitable technique that inhibits the heterotrophic bacterial activity on colonized PAC without affecting its adsorptive properties (i.e. adsorption capacity and kinetics). This chapter is a paper published in *Environmental Technology*. Supplementary information is provided in APPENDIX 2.

GAMMA IRRADIATION: A METHOD TO PRODUCE AN ABIOTIC CONTROL FOR BIOLOGICAL ACTIVATED CARBON

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ABSTRACT

The aim of this paper was to investigate the feasibility of using gamma irradiation to inhibit the microbial activity of biological powder activated carbon (PAC) without impacting its adsorptive properties. First of all, the range of dose of gamma rays required to produce abiotic PAC was selected on the basis of heterotrophic plate counts (HPC) inactivation and methylene blue (MB) adsorption kinetics. Doses inferior to 10 kGy were not sufficient to inhibit the culture of heterotrophic bacteria. On the other hand, doses superior to 15 kGy were demonstrated to affect the adsorption rate of MB. Consequently, a dose comprised between 10 and 15 kGy was selected for further investigation. In order to validate the adequacy of the range of dose (i.e. 10-15 kGy), adsorption characteristics were tested by monitoring the removal kinetics of refractory dissolved organic carbon (RDOC). No significant differences were observed between irradiated and non-irradiated biological PAC for the adsorption of RDOC. Irradiated, non-irradiated and virgin PAC were also evaluated in terms of abundance of viable (using the LIVE/DEAD *Bac*Light™ method) bacteria and in terms of heterotrophic biomass activity. The results of the *Bac*Light™ method demonstrated that attachment of the biofilm on the PAC was not impacted by the irradiation and heterotrophic activity measurements demonstrated that the later could be radically reduced in the range of dose selected. In conclusion, when using a proper dose, the gamma irradiation of colonized activated carbon drastically reduced the heterotrophic activity on activated carbon without significantly impacting its adsorptive behaviour.

KEYWORDS

Activated carbon - Gamma irradiation - Abiotic control - Adsorption - Biodegradation

4.1 Introduction

Maintaining stable drinking water quality during water transit in distribution systems is an important challenge for water utilities. In this context, an increasing number of water treatment plants have decided to rely on the use of activated carbon-based processes. These processes allow removing dissolved biodegradable substrates that promote bacterial regrowth in distribution systems. Others may also elect to use these processes for the reduction of chlorine demand, precursors of chlorinated disinfection byproducts, taste and odors and algal toxins.

Initially developed for their adsorption capacity, granular activated carbon (GAC) filters are now often operated as biological activated carbon (BAC) filters in order to reduce operation and maintenance costs (Prévost et al., 2005). More recently, alternative processes combining low pressure membrane filtration with biological powder activated carbon (PAC) have also been proposed as an alternative to BAC/GAC filters (Stoquart et al., 2012). The objective of these biological processes is to favor the development of a biofilm hosting a consortium of heterotrophic and nitrifying bacteria acclimated to the biodegradation of organic carbon and to the oxidation of ammonia into nitrates. However, both biodegradation and adsorption mechanisms occur simultaneously within activated carbon-based processes used for organic carbon and micropolluants removal (Persson et al., 2007; Stoquart, 2011; Wang et al., 2007). Discriminating the respective contributions of biotic and non-biotic mechanisms in these processes is crucial to assess the proper fate of pollutants, particularly in the case of compounds adsorbable but also amenable to biological oxidation. For instance, Wang et al. (2007) found that adsorption accounted for 70% of the overall removal of microcystin-LR in BAC filters, while microcystin-LA was mainly biodegraded (60%). Such information allows the development of mathematical models and the optimization of operational strategies, and ultimately the enhancement of the process. Yet the relative importance of biotic and non-biotic phenomena remains unknown. Consequently, abiotic controls need to be included in any scientific research. However, this is a challenging task as it is difficult to neutralize the biological activity of activated carbon samples without modifying their adsorptive characteristics.

Various methods have been proposed in the scientific literature to eliminate microbial activity, especially while studying soils microbiology (Trevors, 1996). However, all the techniques tested (e.g., autoclaving, treatment with sodium azide, gamma-irradiation, air drying) altered the chemical and physical properties of the samples (McNamara et al., 2003; Wolf et al., 1989). While sodium azide (NaN_3) is amongst the most common strategy evaluated, bacteria are not equally impacted by this compound. Moreover, adding NaN_3 is likely to increase the ionic strength of the sample, and thus modify the adsorption of dissolved compounds (Lotrario et al., 1995). Finally, interactions with herbicides were observed, affecting the accurate evaluation of their sorption (Chefetz et al., 2006). Autoclaving has also been evaluated as a mean to sterilize BAC samples (Wang et al., 2007). However, autoclaving was shown to lead to an important decrease (55%) in the specific surface area of soil samples (Lotrario et al., 1995) and an increase

of the Freundlich adsorption coefficients (Shaw et al., 1999) of soil samples. Moreover, Berns et al. (2008) showed that autoclaving was responsible for structure modifications of exopolysaccharides, which could potentially be responsible for a loss of integrity of the biofilm and its subsequent release from the surface where it is attached. This modification to the PAC surface could lead to the reopening of previously hidden adsorption sites. Finally, while studying fluidized bed reactors, Zhao et al. (1999) irradiated virgin granular activated carbon samples with gamma rays in order to sterilize their activated carbon. No significant impact of the gamma irradiation on the toluene adsorption capacity of their samples was observed at the applied dose (20 kGy). To the best of our knowledge, there is currently no published demonstration of an ideal method that inhibits the microbial activity on activated carbon without impacting its adsorption characteristics (i.e., capacity and kinetics). The least destructive method has thus to be chosen carefully and depends on the objective of the sterilization. Amongst all techniques, gamma-sterilization seems thus to emerge as the technique with the highest potential.

Gamma-sterilization was extensively studied for soils sterilization and appeared to have the lowest impact on soil samples (Berns et al., 2008; McNamara et al., 2003). The gamma irradiation is commonly applied in the food industry and the health sector for sterilization purposes. The gamma rays are high-energy photons commonly produced by the radioactive decay of ^{60}Co. In water matrices, energy from photons is transferred to electrons, leading to the ionization of the medium and the generation of highly-reactive intermediates such as hydroxyl radicals, protons and hydrated electrons (Taghipour, 2004; Thompson et al., 2000). These intermediates inhibit bacterial growth by modifying the structure of proteins, DNA and RNA which subsequently impacts the metabolic processes (Kent, 1994; Thornley, 1963).

In this study, the gamma irradiation is evaluated as a potential technique to generate an abiotic control for colonized activated carbon. First, the selection of the adequate dose of gamma irradiation was based on its ability to sterilize the PAC (in terms of elimination of heterotrophic plate counts (HPC)) without affecting its adsorptive behavior (in terms of methylene blue (MB) adsorption kinetics). Once the appropriate dose of gamma rays established, the biomass viability and activity on biological PAC were then evaluated before and after gamma irradiation using viable counts (i.e., *Bac*Light™ method) and potential heterotrophic activity methods (i.e., potential ^{14}C-glucose respiration rate and potential acetate uptake rate). The effect of irradiation

on refractory dissolved organic carbon (RDOC) adsorption kinetics was also investigated in order to confirm the MB results.

4.2 Material and Methods

4.2.1 Powder activated carbon

A wood-based PAC (PicaHydro LP39) was colonized in a hybrid membrane process pilot described in details in a previous paper (Léveillé et al., 2013). The pilot was fed with settled water from the Ste-Rose drinking water treatment plant (Laval, Qc). Low pressure membranes were immersed in a 5 and 10 g dry weight (dw) L^{-1} PAC suspension. The PAC age was maintained respectively at 10 and 60 days, which allowed PAC colonization by heterotrophic and autotrophic bacteria. The age of the PAC was maintained stable by purging daily a fraction of the PAC and replacing it by the same amount of virgin PAC.

4.2.2 PAC irradiation

The PAC suspension was sampled from the pilot plant in Ste-Rose (Laval, Qc, Canada). The suspension was filtered on a paper filter (Whatman #41). Dry weights of the PAC cake were evaluated in triplicate according to the 2540 B technique of the Standard Methods (American Public Health Association (APHA) et al., 2005). The PAC cake was resuspended in UF filtered (i.e. ultrafiltration) water from the pilot plant in order to reach a target concentration of 50 g dw PAC L^{-1}. The concentrated suspension (1 L) was then exposed to gamma irradiation with incremental doses of 5 kGy ranging from 0 to 25 kGy (C-188 ^{60}Co source, Underwater Calibrator-15A) in Nordion Inc. Facilities (Laval, Qc, Canada).

4.2.3 Evaluation of the biomass viability on PAC

4.2.3.1 Heterotrophic plate counts (HPC).

Samples were first homogenized in a blender following the method developed by Camper et al. (1985a). A mass of 1 g of PAC wet weight (ww) as well as a mixture of Zwittergent (10^{-6} mol L^{-1}), EGTA (ethylene glycol tetraacetic acid, 10^{-3} mol L^{-1}), Tris-buffer (0.01 mol L^{-1}, pH 7.0) and peptone (0.1%) were mixed in a blender at 16 000 rpm for 3 min at 4 °C. Homogenized samples were analysed in duplicate on R2A agar (incubated 7 days at 20^{o}C) using the membrane filtration

technique (9215 D) of the Standard Methods (American Public Health Association (APHA) et al., 2005). HPC measurements are expressed as Log_{10} CFU (g dw PAC)$^{-1}$.

4.2.3.2 BacLight™ measurements

An epifluorescence staining method using the LIVE/DEAD® Bacterial Viability Kit (*Bac*Light™) was applied to qualitatively estimate the physical integrity of the biofilm at the surface of the PAC. Both *Bac*Light™ stains (i.e., SYTO 9 and propidium iodide) were mixed together and kept protected from light at 20°C. A 3 µL *Bac*Light™ stock solution was added to 1 mL of diluted PAC suspension withdrawn from the pilot plant. Both stains differ in their spectral characteristics and in their ability to penetrate the viable cells. The membrane-permeable SYTO 9 dye labels cells with green fluorescence while the membrane-impermeable propidium iodide labels membrane-compromised bacteria with red fluorescence. Samples were incubated in the dark at room temperature for 15 min before observation. The stained sample was filtered through a black 0.2 µm Nuclepore polycarbonate filter. The filter was mounted in *Bac*Light™ mounting oil. An Olympus microscope equipped with a mercury lamp, a 470–490 nm excitation filter, and a 520-nm barrier filter were used. Viable cell counts are expressed as the number of green-stained bacteria per gram of dry activated carbon, while total cell counts are expressed as the sum of both the green and the red-stained bacteria per gram of dry activated carbon.

4.2.4 Evaluation of the potential activity of heterotrophic biomass on PAC

4.2.4.1 Potential glucose respiration (PGR) rate

This method was adapted from the potential glucose respiration technique developed by Servais et al. (1991) to evaluate the heterotrophic activity of biomass fixed on the surface of GAC from biological filters. This method is based on the measurement of the production of $^{14}CO_2$ due to the mineralization at 20°C of ^{14}C-glucose added at a saturating concentration. The adaptation of the method lays in the fact that 1 g ww of PAC sample was used to evaluate the potential activity of the biomass (as opposed to 2 cm^3 of GAC in the original method). The amount of glucose mineralized was evaluated in triplicate and expressed in nmol ^{14}C-glucose respired (g dw PAC)$^{-1}$ h^{-1}.

4.2.4.2 Potential acetate uptake (PAU) rate

This method evaluates the maximum uptake rate of acetate achieved by the active biomass fixed on PAC. A sample of PAC (10 g ww) was incubated at 20^{o}C on an orbital shaker (approximately 150 rpm) in 500 mL of Milli-Q water amended with an excess acetate solution (15 mg Na-acetate L^{-1}) and nutrients to maintain a C :N :P ratio of 100 :10 :1. Preliminary assays had confirmed that acetate uptake was independent of initial acetate concentration (i.e., zero order kinetics) when the latter was added in excess. The depletion of acetate was monitored for 24 h by sampling 40 mL of the PAC suspension. Samples were immediately filtered on a 0.45 µm PES membrane previously rinsed with 1 L of Milli-Q water. Acetate concentration was determined by ion chromatography (Dionex Corporation, Sunnyvale, U.S.A.). The apparatus was equipped with a IonPac AS18 column and suppressed conductivity detection. The EluGen® EGC-KOH was used as eluent. Acetate uptake rates were calculated by linear regression on the first hours of the assay for colonized PAC in order to reach a linear regression and for 24 h for virgin PAC. Specific PAU rates are expressed in mmol of acetate consumed (g dw PAC)$^{-1}$ h^{-1}.

4.2.5 Evaluation of the adsorption kinetics

4.2.5.1 Methylene blue adsorption kinetics

MB has often been used as a non-biodegradable surrogate (Ferreira-Leitão et al., 2007) for organic matter in adsorption studies (Perry et al., 2005). A 10^{-5} mol L^{-1} solution of MB was prepared in Milli-Q water. Since pH influences MB adsorption (Wang et al., 2005), pH was set to 7.0 using a 1 mol L^{-1} phosphate buffer. A mass of 0.0064 g ww PAC was resuspended in 200 mL of the MB solution and maintained at 20°C under constant agitation at approximately 150 rpm. Subsamples were collected at increasing contact times (i.e., 1, 5, 20, 40, 60 minutes and then every hour) over a period of 7 h and were immediately centrifugated at 9633 *g* for 5 min (Heraeus Pico 17, Thermo Electron Corp., Karlsruhe, Germany). MB concentration was measured in the supernatant using spectrophotometry at 665 nm.

4.2.5.2 RDOC adsorption kinetics

RDOC adsorption kinetics were monitored in PAC batch reactors including either 1 or 10 g dw PAC L^{-1}. Replicate assays were conducted using both settled and raw waters from the Ste-Rose drinking water treatment plant (Laval, Qc). The depletion of RDOC concentration was monitored

over 60 min at 20°C by sampling 125 mL of the PAC suspension at increasing contact times (i.e., 1, 5, 10, 15, 30 and 60 min). Samples were immediately filtered on a 0.45 µm PES membrane previously rinsed with 1 L of Milli-Q water. Dissolved organic carbon (DOC) was measured with a TOC-meter (Sievers 5310 C). Biodegradable DOC (BDOC) analysis were completed using the method adapted from Servais et al. (1989) as described by Markarian et al. (2010). RDOC concentrations were obtained by substracting BDOC from DOC measurements and are expressed in mg C L^{-1}.

4.2.5.3 Modeling

A pseudo second-order model (Eq. 4-1) was used to describe the adsorption kinetics (Tsai, Chang, et al., 2004) :

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad \text{Eq. 4-1}$$

where q_t is the adsorption capacity (in mg (g dw PAC)$^{-1}$), q_e is the equilibrium adsorption capacity and k (in g dw PAC mg $^{-1}$ h^{-1}) is the pseudo second-order rate constant. After integration and linearization, the parameters k and q_e can be obtained from the intercept and slope of the plot of (t/q_t) against t (Tsai, Chang, et al., 2004). Indeed, the pseudo-second order kinetic model has allowed to describe accurately the adsorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions (Ho, 2006). The main assumption of this model is that chemisorption (i.e., sorption involving sharing or exchange of electrons between adsorbent and adsorbate) is the rate-limiting step. Since the adsorption capacity and the rate constant can be determined easily from the equation without any prior parameter estimation, it is nowadays the expression most commonly used for modeling adsorption kinetics (Wu et al., 2009).

4.3 Results and discussion

Proper inhibition of the biomass activity on PAC requires determining the minimum and maximum doses of irradiation that can be applied on the samples. The minimum dose is the dose of gamma rays required to suppress the biomass activity in the samples. The maximum dose of irradiation is defined as the maximum dose of gamma rays that could be applied without modifying the adsorptive properties of the sample. Our research hypothesis is that such range of

doses exists (i.e., biological activity can be minimized without significantly interfering on adsorption).

HPC and MB adsorption kinetic were the methods selected to assess the impact of gamma rays (doses ranging from 0 to 25 kGy) on the culturability and the adsorptive behavior of PAC samples, respectively. These methods were selected based on their efficiency in terms of cost, time and feasibility. Results gathered enabled to determine rapidly the adequate range of dose recommended to produce an abiotic control of colonized PAC. In order to validate the recommended range of gamma ray doses, new samples were submitted to irradiation in this range, and activity-based methods (i.e., PGR and PAU rates) were used to confirm the impact of irradiation on the biomass activity. In parallel, the removal kinetics of RDOC were monitored in order to confirm the impact of irradiation on the adsorption of the natural organic matter.

4.3.1 Selection of the appropriate dose of gamma irradiation

4.3.1.1 Minimum dose of gamma rays

HPC enumerations were performed on PAC colonized for a 60-d period and irradiated with doses ranging from 0 to 25 kGy. Results presented in Table 4-1 demonstrate that a dose of at least 10 kGy is required to inhibit the formation of colonies on R2A agar. A dose of 10 kGy is higher than the 0.35 kGy value previously suggested for achieving 4 $\log_{10}$ units of *E. coli* inactivation in axenic cultures (Thompson et al., 2000). However, in that case, the conditions of irradiation were completely different. Only one type of microorganism (*E. coli*) was irradiated in a suspension saturated in dissolved oxygen. The oxygen saturating conditions (Thompson et al., 2000), the absence of shielding effect (McNamara et al., 2003) and the homogeneity of the bacteria population could explain the much lower dose required for sterilization. On the opposite, when irradiating samples with a complexity closer to that of colonized activated carbon (e.g., soil samples), the dose found here appears to be consistent with the scientific literature. When applying a dose of gamma irradiation comprised between 10 and 25 kGy on soil samples, most bacterial groups were found to be no longer culturable (McNamara et al., 2003).

Table 4-1 : Heterotrophic plate counts and total and viable cell counts (using the *Bac*Light™ technique) on colonized 60-d PAC exposed to gamma rays doses ranging from 0 to 25 kGy.

Dose applied (kGy)	Total cell counts (HPC) (Log_{10} CFU (g dw PAC)$^{-1}$)	Total cell counts (*Bac*Light™) (Log_{10} bact (g dw PAC)$^{-1}$)	Viable cell counts (*Bac*Light™) (Log_{10} bact (g dw PAC)$^{-1}$)
0	7.5	10.5	10.3
5	3.8	10.5	10.3
10	< L.D.	10.5	10.2
15	< L.D.	10.5	10.1
20	< L.D.	N.A.	N.A.
25	< L.D.	10.5	10.2

* L.D. = 200 CFU (g dw PAC)$^{-1}$

4.3.1.2 Maximum dose of gamma rays

MB adsorption kinetic was studied using irradiated 60-d colonized PAC (0-25 kGy). The mass of MB adsorbed per mass of adsorbent (i.e. q_t) was calculated and expressed in mg MB (g dw PAC)$^{-1}$. These results were modeled according to a pseudo second-order model (Eq. 1; $R^2 > 0.96$) in order to assess the adsorption capacity at equilibrium (q_e) and the kinetic constant (k). Results are presented in Figure 4-1. For all gamma doses investigated, the PAC adsorption capacity (i.e. q_e) was not influenced by the irradiation (i.e. no significant linear regression between q_e and the irradiation dose was observed, p-value > 0.05). q_e values fluctuated randomly in the range of 290-360 mg MB (g dw PAC)$^{-1}$. On the other hand, the MB adsorption kinetics were noted to increase with the dose of irradiation (p-value = 0.024). It should be noted that the k-value corresponding to a 10 kGy dose of irradiation appeared to be an outlier. Consequently, this result will not be considered for the rest of the discussion. While a 5 kGy dose did not affect the k-value, irradiating the sample with a dose of 15 kGy led to a 1.5-fold increase in the MB adsorption rate (k). This observation suggests that high doses will modify the surface properties in such a way that diffusion of MB within activated carbon is increased. Potential release of biofilms which were blocking adsorption sites could explain such observation. Figure 4-2 depicts the predicted percentages of MB removal for a dose of gamma rays ranging from 0 to 25 kGy in function of the contact time. Predictions of the potential removal of MB are presented for 1 h, the highest

realistic contact time considered in the PAC contactor of a hybrid membrane process. These predictions were realized by considering a pseudo second-order adsorption kinetic, the absence of modification of the adsorption capacity (i.e. the average value of 319 mg MB (g dw PAC)$^{-1}$ from Figure 4-1 was used for q_e) and by using the *k*-values presented in Figure 4-1. Curves presented in the Figure 4-2 demonstrate that while a 5 kGy dose virtually left unchanged the percentage of MB removed in 1 h, irradiating with a 15 kGy dose increased the amount of MB removed by 8% for the same contact time. Doses superior to 15 kGy impacted the amount of MB removed in 1 h by increasing its adsorption by more than 10%. The results of a previous study Zhao et al. (1999) demonstrated that a slightly higher dose (20 kGy) than that applied in our study do not modify the capacity of toluene adsorption of a virgin GAC sample. The absence of biofilm on the GAC tested could explain the discrepancy between the doses proposed in both studies. In conclusion, doses inferior to 15 kGy should be targeted in order to limit the impact of the irradiation on the adsorption kinetics of colonized PAC.

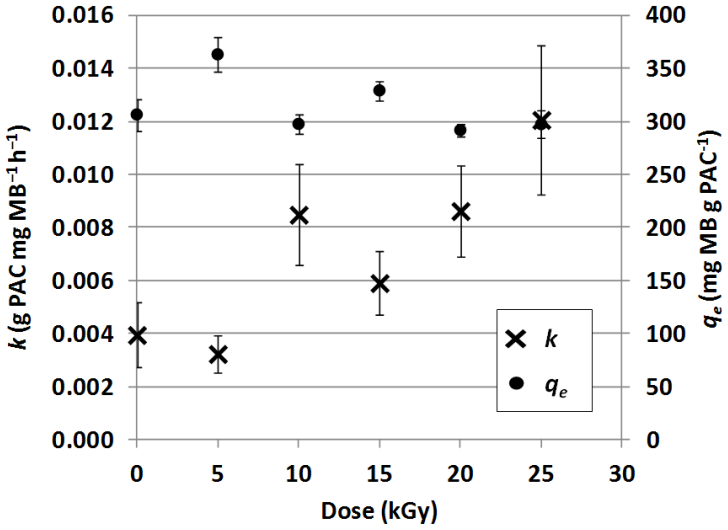

Figure 4-1 : Pseudo second-order kinetics constants *k* and q_e obtained for MB adsorption on 60-d PAC exposed to gamma rays doses ranging from 0 to 25 kGy.

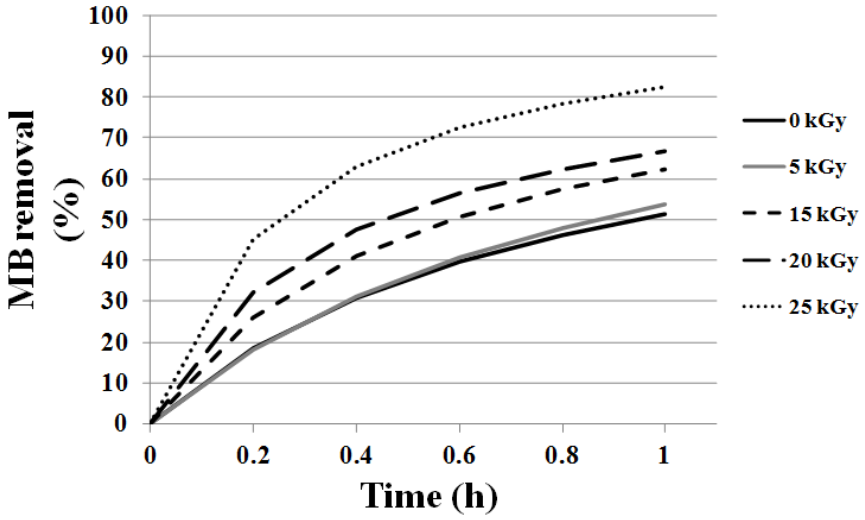

Figure 4-2 : Predicted percentages of MB removal for a dose of gamma rays ranging from 0 to 25 kGy in function of the contact time. Predictions were based on pseudo second-order kinetic model for 1 h maximum. The 10 kGy curve was excluded.

4.3.2 Impact of irradiation on biomass viability and activity on colonized PAC

Although the HPC measurements demonstrated that irradiation was an effective method to suppress the ability of bacteria to multiply on a solid culture medium (see Table 4-1), additional information was required to confirm that biomass metabolic activity had also been significantly inhibited by this treatment. Therefore, the impact of gamma irradiation on the activity of heterotrophic biomass was evaluated using more advanced methods such as the PGR and PAU rates. Figure 4-3 indicates that gamma irradiation (dose of 13 kGy) reduced by 83% the PGR rate of colonized PAC while the PAU rate was reduced by 71%. For this dose, HPC measurements were below detection limit (i.e. < 200 CFU (g dw PAC)$^{-1}$). The HPC as well as the PGR and PAU rates were also evaluated on new PAC (i.e. non-colonized PAC) (see Figure 4-3). These measurements are used as controls to demonstrate the impact of irradiation on the activity of the heterotrophic biomass. Submitting colonized PAC to gamma irradiation decreased drastically its biological activity by preventing the multiplication of hetereotrophic bacteria and by hindering the oxidation of easily assimilable compounds such as glucose and acetate. However, a residual potential activity of the biomass was measured with both PAU and PGR methods.

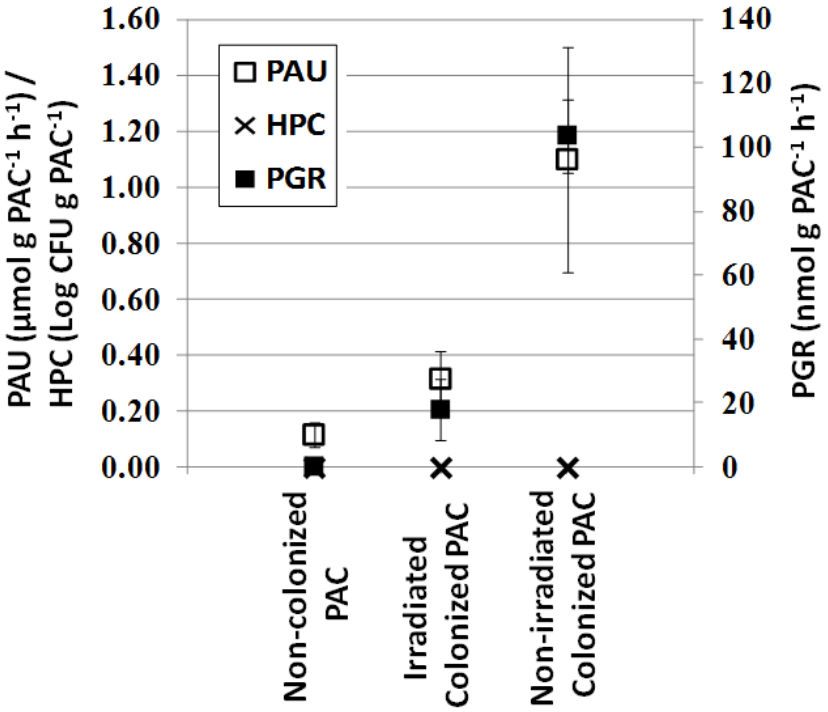

Figure 4-3 : Measurements of bacterial abundance and potential heterotrophic biomass activity on virgin (non-colonized), non-irradiated 60-d colonized PAC and irradiated 60-d colonized PAC (dose of 13 kGy). The methods used were: HPC in Log_{10} CFU (g dw PAC)$^{-1}$, PGR in nmol (g dw PAC)$^{-1}$ h^{-1}, PAU in µmol (g dw PAC)$^{-}$1 h^{-1}. Standard deviations are represented with the whiskers bars.

There was no visible effect of the gamma-irradiation of the 60-d PAC sample on the viable (p-value = 0.11) and total (p-value = 0.30) cell counts expressed in Log_{10} bact per g dw PAC obtained with the LIVE/DEAD *Bac*Light™ method (see Table 4-1). Indeed, radiolysis products of gamma irradiation are strong oxidants that damage DNA by inducing single and double-strand breaks, base-free sites and by altering the DNA bases (Henner et al., 1982). Thus, this result suggests that no significant cell lysis occurred during the irradiation treatment. In addition, the epifluorescence observations (Figure A-2.1, Supplementary Information) suggest that gamma rays did not physically alter the biofilm as no major detachment of biomass was observed in the conditions tested (dose of 15 kGy). This is a desirable characteristic for the abiotic control of colonized activated carbon as it is hypothesized that biofilm detachment may influence the diffusion of natural organic matter inside the PAC particles by increasing the amount of available adsorption sites.

4.3.3 Impact of irradiation on the adsorption of the organic matter by PAC

The impact of the irradiation on the PAC adsorptive characteristics was further studied by monitoring RDOC adsorption kinetics. The latter were monitored during laboratory assays conducted with concentrations of 1 and 10 g dw PAC L^{-1} in settled (coagulated with alum) and raw waters using 10-d and 60-d colonized PAC irradiated (13 kGy) and not irradiated (see Table 4-2). As RDOC can only be removed by PAC adsorption, these results confirmed the conclusions obtained with MB at doses between 10-15 kGy: no statistically significant differences were observed for the parameters evaluated by the pseudo second-order model (p-values for q_e and k were 0.74 and 0.40, respectively). It should be noted that q_e-values were increased by an order of magnitude when using ten times less PAC. This phenomenon can be explained by the fact that during the assays, the adsorption kinetic was probably limited by the amount of adsorbable RDOC rather than by the amount of adsorbent. When using a smaller concentration of PAC, it appears that its usage is maximized. By lowering the concentration of the PAC in the reactors, absolute removal was decreased but potential of the PAC was better exploited. In addition, k-values were shown to vary on a logarithmic scale depending on water type and PAC ages. Therefore, this observation supports the idea that the 1.5-fold variation in k value observed earlier for MB adsorption is in fact a low variation on a logarithmic scale (0.18 Log). Finally, modeling the impact of the irradiation on the efficiency for the RDOC removal allowed confirming the previous results. For all the operating conditions presented Table 4-2, the impact of the irradiation on RDOC removal after 1 h of contact time was inferior to 0.11 mg C L^{-1}, which corresponds to the usual accuracy of the RDOC measurements. In summary, the adsorption kinetics of MB and RDOC on PAC were marginally impacted by gamma irradiation (i.e. at doses of 10 to 15 kGy). This is in agreement with a previous study recommending gamma irradiation as a reliable sterilization technique for soils (Lotrario et al., 1995). These authors concluded that gamma irradiation had a minimal effect on the size distribution of soil particles and on their BET surface area.

Table 4-2 : Kinetics constants calculated for RDOC adsorption on PAC with non-irradiated and irradiated PAC (13 kGy) of 10-d and 60-d in settled (SW) and raw (RW) water.

Conditions	q_e	$q_{e,irradiated}$	k	$k_{irradiated}$
	(mg RDOC (g dw PAC)$^{-1}$)		Log_{10} (g dw PAC (mg RDOC)$^{-1}$ h^{-1})	
10 g 60-d PAC L^{-1}, SW	0.02	0.06	3.1	3.6
10 g 60-d PAC L^{-1}, RW	0.36	0.38	2.1	2.3
10 g 10-d PAC L^{-1}, SW	0.13	0.1	2.6	2.9
10 g 10-d PAC L^{-1}, RW	0.46	0.41	2.1	2.3
1 g 60-d PAC L^{-1}, SW	0.44	0.73	2.0	1.3
1 g 10-d PAC L^{-1}, SW	1.31	0.81	1.2	1.7
p-value	0.73		0.40	

In this study, the optimal dose of irradiation was comprised between 10 and 15 kGy. This range of doses allowed to reduce the active biomass but did not entirely inhibit its metabolic activity. However, the adsorption kinetics demonstrated that applying higher doses of gamma rays would have led to an increased adsorption of natural organic matter and MB.

Our results demonstrated that the irradiation dose should remain as low as possible in order to limit its effect on the physical and chemical properties of the activated carbon. However, among microbial populations, resistance to gamma beams varies and resistant populations are also met in non-extreme environments (Daly, 2000; Thornley, 1963). Furthermore, water alkalinity can act as a scavenger of radiolysis products (Thompson et al., 2000), thereby modifying the dose of irradiation necessary for the inactivation of a given sample. Sample size also influences the dose required (e.g. a shielding effect occurs when irradiating large samples). Consequently, it is advised to validate the dose of irradiation for each new project involving the inhibition of activated carbon heterotrophic activity. The use of MB adsorption and PAU method are recommended to evaluate the optimal dosage of gamma rays as the former is a simple method that provided information coherent with NOM adsorption while the latter, although more complex than HPC, provided a better evaluation of the heterotrophic activity on the colonized PAC. Future work should evaluate if the optimal dose range (10-15 kGy) identified for heterotrophic biomass could be extended to the case of the autotrophic biomass fixed onto activated carbon. Finally, irradiating PAC samples remains costly and its accessibility is not

guaranteed. Drawbacks of less expansive methods (e.g. autoclaving) have been observed in soil samples. However, comparing their efficiency on PAC samples could be of great interest to potentially reduce spending.

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CHAPTER 5 ARTICLE 4 – AMMONIA REMOVAL IN THE CARBON CONTACTOR OF A HYBRID MEMBRANE PROCESS

This chapter presents the first out of three papers devoted to the study of the performance of HMPs for the removal of dissolved compounds. In this chapter, ammonia is the dissolved compound of concern. The removal kinetics occurring in the PAC contactor of HMPs are monitored under various operating conditions (various temperature, PAC age, PAC concentration, water matrix). Significant ammonia adsorption was evidenced on both virgin and aged PAC. However, nitrification was crucial to reach the complete ammonia removal observed at 22°C on aged PAC. Ammonia adsorption and nitrification are described in a kinetics model that evidences the relative importance of these mechanisms under natural ammonia concentration as well as when facing a sudden increase in ammonia concentration. This chapter is paper accepted for publication in *Water Research*.

AMMONIA REMOVAL IN THE CARBON CONTACTOR OF A HYBRID MEMBRANE PROCESS

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ABSTRACT

The hybrid membrane process (HMP) coupling powdered activated carbon (PAC) and low-pressure membrane filtration is emerging as a promising new option to remove dissolved contaminants from drinking water. Yet, defining optimal HMP operating conditions has not been confirmed. In this study, ammonia removal occurring in the PAC contactor of a HMP was simulated at lab-scale. Kinetics were monitored using three PAC concentrations (1-5-10 g L^{-1}), three PAC ages (0-10-60 days), two temperatures (7-22°C), in ambient influent condition (100 µg $N–NH_4$ L^{-1}) as well as with a simulated peak pollution scenario (1000 µg $N–NH_4$ L^{-1}). The following conclusions were drawn: i) Using a colonized PAC in the HMP is essential to reach complete ammonia removal, ii) an older PAC offers a higher resilience to temperature decrease as well as lower operating costs; ii) PAC concentration inside the HMP reactor is not a key operating parameter as under the conditions tested, PAC colonization was not limited by the available surface; iii) ammonia flux limited biomass growth and iv) hydraulic retention time was a critical parameter. In the case of a peak pollution, the process was most probably phosphate-limited but a mixed adsorption/nitrification still allowed reaching a 50% ammonia removal. Finally, a kinetic model based on these experiments is proposed to predict ammonia removal occurring in the PAC reactor of the HMP. The model determines the relative importance of the adsorption and biological oxidation of ammonia on colonized PAC, and demonstrates the combined role of nitrification and residual adsorption capacity of colonized PAC.

KEYWORDS

Drinking Water - Hybrid membrane process - colonized PAC - Nitrification - Ammonia adsorption - Pseudo-second order kinetics

5.1 Introduction

Ammonia is commonly found in surface waters and groundwater. If ammonia is not removed during drinking water (DW) treatment, its presence at the final chlorination stage will be responsible for an increase in chlorine demand. Furthermore, its oxidation by free chlorine may yield taste and odor issues due to trichloramine formation. In DW production, both chemical and

biological oxidation processes can be applied to remove ammonia. Biological treatment of DW has gained acceptance in the last 20 years because of its attractive cost and ability to meet multiple water quality criteria (e.g. reducing organic carbon concentration allowing lower disinfection byproducts formation at the post chlorination stage and DW biostability in distribution systems) (Prévost et al., 2005). Ammonia removal by nitrification (Andersson et al., 2001) is another advantage of biological treatment.

The hybrid membrane process (HMP), which couples a high concentration powdered activated carbon (PAC) contactor with low-pressure membranes, stands out as one of the most promising solutions to reach the targeted low concentrations of dissolved contaminants (Kim et al., 2005). Most of the published literature on HMPs is based on the use of PAC as adsorbent (Stoquart et al., 2012), which allows efficient removal of natural organic matter (NOM) as well as trace organic contaminants (e.g. algal toxins, pesticides, pharmaceuticals) by maintaining a low PAC retention time (PAC age < 7-d). Although adsorption of ammonia on activated carbon is typically considered marginal (Bandosz et al., 2009), increasing the PAC retention time in the carbon contactor allows its colonization by heterotrophic and nitrifying bacteria (Stoquart et al., 2013). Under such operating condition, it is hypothesized that NOM and ammonia removals are achieved by a combination of adsorption and biodegradation. Increasing the PAC age offers the additional benefit of drastically reducing the operating costs by minimizing the virgin PAC consumption rate.

Under warm water conditions (i.e. superior to 8.5°C as defined in Léveillé et al. (2013)), nearly complete ammonia removal was observed inside the reactor of a HMP containing 10 g L^{-1} of colonized PAC . However, as temperature drops, the metabolism of nitrifying bacteria slows down (Andersson et al., 2001) and the efficiency of the HMP using colonized PAC is reduced (Suzuki et al., 1998). Nevertheless, the HMP was demonstrated to have the potential to enhance its performance in cold waters by increasing the PAC concentration and/or contact time (Markarian et al., 2010). Adsorption and, to a larger extent, nitrification are the mechanisms potentially responsible for ammonia concentration mitigation in the HMP. However, no information is presently available in the literature to distinguish the respective contribution of both mechanisms to ammonia removal. Previous studies highlighted that PAC age, PAC concentration and the hydraulic retention time (HRT) were key variables to predict the removal of dissolved compounds (Markarian et al., 2010). We hypothesize that these variables as well as

temperature influence the relative importance of both adsorption and nitrification. Discriminating the role of each mechanism is thus crucial to describe the performance of the HMP.

In this study, experiments simulating the kinetics of ammonia removal occurring in the PAC reactor of a HMP were conducted at lab-scale. The contact time, the temperature, the age and the PAC concentration inside the reactor were the parameters under investigation. Efficiency of the PAC contactor was studied using settled water (SW) originating from a full scale surface water treatment plant. Based on the experimental data, a kinetic model was developed accounting both for adsorption and nitrification. The proposed model provides a better understanding of the process and thus will allow enhancing the quality of the treated water while reducing the operating costs.

5.2 Material and Methods

5.2.1 Powdered activated carbon samples

A wood-based PAC (Picahydro LP 39) was used (median diameter 15-35 µm). This meso- to macroporous PAC was chosen to favor biomass growth. PAC colonization was realized in two industrial HMP pilot facilities described in Léveillé et al. (2013). Briefly, ultrafiltration membranes were immersed in a PAC suspension. Daily purges of a fraction of the PAC content and its replacement by the same amount of virgin PAC allowed maintaining the average age of PAC stable in the carbon contactor of the pilot-plant. Ages referred to in this manuscript thus correspond to the average PAC retention time of a distribution of ages in the suspension. Theoretical age distributions are presented in Figure 5-1. In both parallel reactors, PAC ages were maintained respectively at 10-d and 60-d with the following targeted operating concentrations: 4 g L^{-1} (3.5±1.2 g L^{-1}) for the 10-d and 10 g L^{-1} (9.8±1.1 g L^{-1}) for the 60-d. These ages allowed the PAC colonization by heterotrophic and autotrophic nitrifying bacteria. Both HMP contactors were operated with a HRT of 67 min. The PAC contactors were fed with settled water from the Ste-Rose DW treatment plant (DWTP) (Laval, Qc, Canada) (pH = 6.77 ± 0.24; turbidity = 0.7±0.1 NTU (method 2130B, (American Public Health Association (APHA) et al., 2012)); UV254 = 0.062±0.009 cm^{-1} (method 5910B, (American Public Health Association (APHA) et al., 2012)); DOC = 3.44±0.24 mgC L^{-1} (method 5310C, (American Public Health Association (APHA) et al., 2012)); alkalinity = 20±2 mg $CaCO_3$ L^{-1} (method 2320B, (American Public

Health Association (APHA) et al., 2012))). The water temperature in the pilot-plant varied with the temperature of the feed water (3°C to 25°C). Operating the PAC contactor under contrasted temperature conditions produced aged PACs acclimated to these temperature conditions.

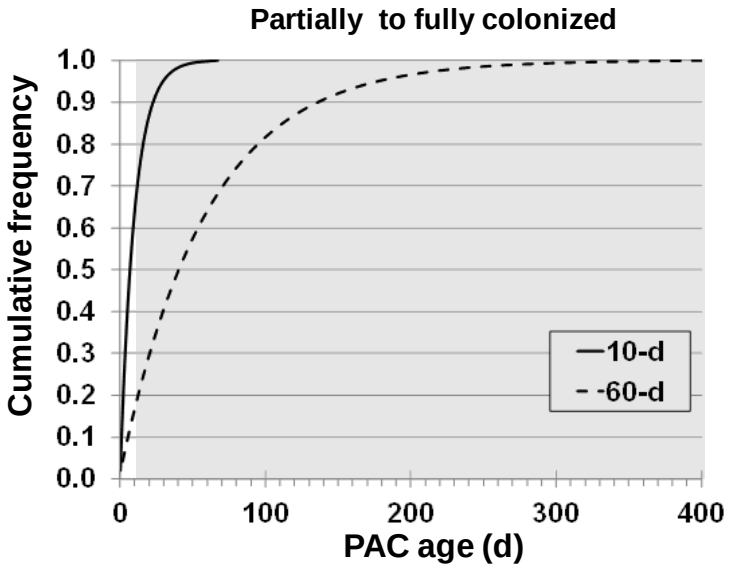

Figure 5-1 : Theoretical cumulative frequency distribution of PAC age for the 10-d and 60-d PAC suspensions.

5.2.2 Potential nitrifying activity (PNA)

This method, initially developed by Kihn et al. (2000) to indirectly estimate the nitrifying biomass fixed on GAC, was adapted for the need of the present study. The production rate of oxidized nitrogen (*i.e.* nitrite and nitrate) in standardized optimal conditions was measured and used as a surrogate to evaluate the sum of ammonia- and nitrite-oxidizing bacterial biomass at the surface of PAC. Colonized PAC was sampled from the pilot-plant and filtered on a 20 µm paper filter (Grade 41, Whatman®) to recover a dense cake of PAC. PAC was cleaned by resuspension in an ammonia-free nitrifying medium to eliminate interferences (Kihn et al., 2000) and then filtered again on Grade 41 paper filter (Whatman®). Cleaned PAC (1 g wet weight) was incubated in duplicate at 30°C for 30 minutes in 5 mL of nitrifying medium (containing 10 mg N-NH_4 L^{-1})(pH = 8). During incubation, the medium was oxygenated by air purified in a sulfochromic acid solution. After incubation, the suspension was filtered through a 0.22 µm MCE syringe filter (Millex®-GS). Concentrations of nitrite and nitrate were measured (Jones, 1984) after 0, 15 and 30 min of incubation. The PNA (in µmol N g^{-1} h^{-1}) corresponds to the slope of the

sum of $N\text{-}NO_3$ and $N\text{-}NO_2$ oxidized plotted against the incubation time. Average standard error (based on errors of incubation time, sampling volume of the solid support, the heterogeneity of the fixed biomass on the solid support and the measurement of the oxidized nitrogen after incubation) was evaluated as 15% of the estimated PNA (Kihn et al., 2000).

5.2.3 Kinetics of ammonia removal

Ammonia kinetic removal studies were performed using suspensions of (i) colonized PAC from the pilot-plant and (ii) virgin PAC neutralized (pH = 7) with a 1M NaOH solution 12-24 hours before the assays. The acclimated PAC suspension was sampled and kept under the same temperature conditions to minimize the potential disturbance of the colonized PAC. Ammonia removal kinetics were monitored immediately upon reception of the PAC samples at the laboratory. The PAC suspensions (i.e. colonized or virgin) were filtered on a 20 µm paper filter (Grade 41, Whatman®) to recover a dense PAC cake. Dry weights (dw) of the cake were evaluated in triplicate with the 2540-B technique (American Public Health Association (APHA) et al., 2012). A portion of the PAC cake was resuspended in 2 L of SW from the Ste-Rose DWTP to achieve the targeted PAC concentration in the reactor (1, 5 or 10 g L^{-1}, dw). Equivalent dosages are defined as "the quantity of PAC renewed to treat a given daily volume of water" (Stoquart et al., 2012). The conditions under investigation spanned a large range of equivalent PAC dosages: from 0.7 mg L^{-1} for the 1 g L^{-1}/60-d condition to 42 mg L^{-1} for the 10 g L^{-1}/10-d condition. The operating conditions tested during these assays are summarized in Table 5-1. Ammonia removal kinetics were studied using ambient SW and SW spiked to reach an initial concentration of 1 mg $N\text{-}NH_4$ L^{-1}. Experiments conducted at a targeted temperature were realized with PAC acclimated at the pilot-plant to that same temperature. PAC concentrations are always expressed as dry weights throughout the manuscript.

Table 5-1 : Tested operating conditions in the simulated PAC contactor at lab-scale

Varying parameters	**Values targeted**	**Values measured ± standard dev.**	**# conditions tested**
Initial ammonia concentration ($\mu g\ N\text{-}NH_4\ L^{-1}$)	100	89 ± 20	2
	1000	984 ± 49	
PAC concentration ($g\ L^{-1}$)	1	1.0 ± 0.1	3
	5	4.9 ± 0.4	
	10	9.7 ± 1.1	
Temperature (°C)	7	7.2 ± 0.9	2
	22	22 ± 1	
PAC age (d)	0	N.A.	3
	10	N.A.	
	60	N.A.	
Total number of unique operating conditions tested			36

N.A. : Not Available

Ammonia concentration was monitored by sampling 50-100 mL of the PAC suspension after contact times of 1, 5, 10, 15, 30 and 60 minutes, 60 minutes being the highest contact time considered realistic for the full-scale operation of the HMP. Samples were immediately submitted to a sequential filtration on a 1.5 µm microfiber glass filter (934-AH, Whatman®) paper filter followed by a 0.45 µm PES filter (Pall Supor®-450) to ensure the immediate separation of the PAC from the water. Ammonia concentration was then measured in triplicate using the indophenol colorimetric method #T90-015 (AFNOR, 1990). Accuracy of the method was 3 µg N L^{-1} in SW (detection limit of 5 µg N L^{-1}). In general, ammonia removal kinetics were followed once for each condition. A few conditions were tested a second time at a one year interval. Results confirmed the high reproducibility of the simulation of the PAC contactor.

5.2.4 Mathematical modeling

Ammonia removal was assumed to be the result of two independent parallel mechanisms: adsorption and nitrification. The modeling of both mechanisms is described in the following sections.

5.2.4.1 Nitrification modeling

Microbial oxidation of ammonia into nitrate is known to be a two-phase process requiring the oxidation of $N\text{-}NH_4$ in $N\text{-}NO_2$ which can be performed by *Nitrosomonas*-like bacteria and by archaea (Niu et al., 2013). Subsequently $N\text{-}NO_2$ is oxidized into $N\text{-}NO_3$ by *Nitrobacter*-like bacteria. Both oxidation processes can be described with a single-limited substrate condition using the Monod-type expression presented in Eq. 5-1. In the complete microbial process of oxidation of ammonia into nitrates, oxidation of ammonia can be assumed as the rate-limiting step (WPCF, 1983).

$$\frac{dS}{dt} = -\mu_{max}\frac{X}{Y_S}\frac{S}{K_S + S} \qquad \text{Eq. 5-1}$$

In Eq. 5-1, dS/dt is the substrate removal rate (in µg N $L^{-1}min^{-1}$), μ_{max} the maximum specific growth rate (min^{-1}), X the bacterial biomass concentration (g cell L^{-1}), Y_S the yield of bacterial mass produced per unit of substrate used (g cell µg N^{-1}), S the limiting substrate (ammonia) concentration (µg N L^{-1}) and K_S the half-saturation constant (µg N L^{-1}).

The initial ammonia concentration remained less than or equal to 1 mg N L^{-1} during all the kinetics monitored. Since the K_S value established in biofilters is comprised between 2 and 8.5 mg N L^{-1} (Chen et al., 2006), the substrate removal rate always remains in the linear portion of the Monod type equation. Eq. 5-1 can thus be simplified ($S<<K_S$) in order to fit a first-order reaction described as:

$$\frac{dS}{dt} = -\frac{\mu_{max}}{K_S}\frac{X}{Y_S}S \qquad \text{Eq. 5-2}$$

The bacterial biomass concentration (*X*) was considered directly proportional to the concentration of PAC in the lab-scale contactor. This assumption is logical since during the experiments, a unique PAC cake was used to adjust the initial PAC concentrations in the lab-scale contactors. We assume that the repartition of the bacterial biomass at the surface of the PAC is homogenous and directly proportional to the PAC concentration (cf. Eq. 5-3). The bacterial biomass fixed on the PAC is expected to vary with the PAC age and HRT, especially since the colonizing concentrations were different in the 10-d and 60-d pilot plant reactors.

$$X = \left[\frac{gcell}{gPAC}\right] \times [PAC] \quad \text{Eq. 5-3}$$

Using Eq. 5-3 in Eq. 5-2 yields Eq. 5-4:

$$\frac{dS}{dt} = -A \times {\theta_{nit}}^{T-20} \times [PAC] \times S \quad \text{Eq. 5-4}$$

In Eq. 5-4, $A = \frac{\mu_{max} \times \frac{gcell}{gPAC}}{Y_S K_S}$ (in L g^{-1} s^{-1}) represents the activity of the nitrifying biomass. An Arrhenius law (${\theta_{nit}}^{T-20}$) is used to reflect the dependence of nitrifying activity on water temperature (Wijffels et al., 1995).

Using the integrated version of Eq. 5-4, the fraction (F_{nit}), which corresponds to the ratio of the amount of ammonia nitrified to the initial amount of ammonia available, can be calculated as:

$$F_{nit} = 1 - \exp^{\left(-A \times {\theta_{nit}}^{T-20} \times [PAC] \times t\right)} \quad \text{Eq. 5-5}$$

5.2.4.2 Adsorption modeling

Pseudo-second order (PSO) models have been widely applied to describe adsorption kinetics in liquid-phase systems (Wu et al., 2009). The PSO model, as used in this manuscript, is presented under the following form:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \text{Eq. 5-6}$$

In Eq. 5-6, q_t is the adsorption capacity (in µg N g^{-1}), q_e the equilibrium adsorption capacity and k_2 the PSO rate constant (in g µg N^{-1} h^{-1}).

A Freundlich adsorption isotherm (Eq. 5-7) was used to define q_e in Eq. 5-6.

$$q_e = K {C_e}^{1/n} \quad \text{Eq. 5-7}$$

In Eq. 5-7, the values of K (in µg N g^{-1} (µg N L^{-1})$^{-1/n}$) and n are the characteristic constants of the system and C_e is the concentration of ammonia in the liquid at equilibrium (in µg N L^{-1}).

Integrating and rearranging Eq. 5-6 and including Eq.5-7 gives Eq. 5-8 in which the fraction F_{ads} corresponds to the ratio of ammonia adsorbed to the initial amount of ammonia in solution:

$$F_{ads} = \frac{[PAC]}{S_0 \times \left(\frac{1}{K C_e^{1/n}} + \frac{1}{t} \times \frac{1}{k_2 K^2 C_e^{2/n}} \right)} \quad \text{Eq. 5-8}$$

As the temperature potentially impacts adsorption capacity and the adsorption kinetics, an Arrhenius Law (i.e θ_{ads}^{T-20}) is added in Eq. 5-8 to give Eq. 5-9:

$$F_{ads} = \frac{[PAC]}{S_0 \times \left(\frac{1}{K C_e^{1/n}} + \frac{1}{t} \times \frac{1}{k_2 K^2 C_e^{2/n}} \right)} \times \theta_{ads}^{T-20} \quad \text{Eq. 5-9}$$

As it can be noted, the modeling of the ammonia adsorption kinetics depends on fitting parameters (K, n, k_2, θ) and on independent variables (t, T, [PAC], S_o). The variable C_e depends on the tested conditions (T, [PAC], S_o) and cannot be controlled independently during an experiment. The following sections explain how this value was derived for the various tested conditions.

Virgin PAC. The C_e -value was considered to be the concentration of ammonia in the water phase obtained after a contact time of approximately 60 minutes, 60 minutes being the longest contact time tested during the kinetics. As will be shown in section 5.3.1.1., adsorption of ammonia on virgin PAC was very fast (<5 min) and independent from the contact time (p-value = 1.00) after 5 min. Therefore, the value of ammonia after 60 min was considered a good proxy of the equilibrium concentration.

Colonized PAC. When modeling ammonia removal on 10-d and 60-d PAC, the concentration of ammonia obtained after a contact time of 60 minutes could not be used to determine the C_e- value as adsorption is not the only process responsible for the decrease of the ammonia concentration.

In cold water, ammonia removal kinetics were monitored in parallel with the production of N-NO_2 and N-NO_3 (analyzed by ionic chromatography using a Dionex ICS-3000 supplied with a UV-detector and an AS40 sampler). Nitrite and nitrate concentration measurements were used to calculate the removal due to nitrification (F_{nit}). The remaining removal was assumed to be the

result of adsorption (F_{ads}). Knowing the fraction of ammonia removed by adsorption, it was simple to back-calculate the equilibrium concentration (C_e) after 60 min. Under warm water conditions (22°C), N-NO_2 and N-NO_3 concentrations were not available. In that case, the experimental F_{ads} was considered to be the same at 7 and 22°C. This approximation was supported by the fact that even if the impact of temperature on adsorption is significant (p-value < 0.01), less than a 10% difference in ammonia adsorption was noted in cold versus warm temperature on virgin PAC (see section 5.3.1.1.).

5.2.4.3 Modeling nitrification and adsorption

The fraction F_{Tot} allows calculating the percentage of ammonia removed by both adsorption and nitrification and corresponds to the sum of F_{nit} and F_{ads}:

$$F_{Tot} = \left(1 - \exp^{\left(-A \times \theta_{nit}{}^{T-20} \times [PAC] \times t\right)}\right) + \frac{[PAC]}{S_0 \times \left(\frac{1}{K C_e{}^{1/n}} + \frac{1}{t} \times \frac{1}{k_2 K^2 C_e{}^{2/n}}\right)} \times \theta_{ads}{}^{T-20} \qquad \text{Eq. 5-10}$$

Parameters of this equation were determined using Statistica 12 (Statsoft, USA) through non-linear estimations based on the least squares method and a Gauss-Newton regression method. Fitting the 1 and 5 g L^{-1}, the 5 and 10 g L^{-1} and the 1 and 10 g L^{-1} datasets gave similar values for the parameters (R-values superior to 0.97). As fitting the 1 and 10 g L^{-1} dataset gave the highest R-value (always >0.99), this approach was favored. The resulting predictive model was validated with the experimental results at 5 g L^{-1}.

5.3 Results

5.3.1 Experimental ammonia removal kinetics

Assays on virgin PAC (0-d) will be presented prior to results conducted on colonized PAC (10-d and 60-d). Operating an industrial scale HMP process with virgin PAC would require its continuous renewal, which is not economically viable. Virgin PAC assays thus served as a control in which adsorption is the only mechanism responsible for ammonia removal (i.e. $F_{Tot} = F_{ads}$).

5.3.1.1 Ammonia removal on virgin PAC

Figure 5-2 presents the ammonia removal kinetics (F_{Tot}) in SW (Figures 5-2a and 5-2b) and in spiked SW (Figures 5-2c and 5-2d) using virgin PAC at 7°C and 22°C. There was no significant impact of contact time on ammonia adsorption on virgin PAC (ANOVA on the entire dataset obtained on 0-d PAC: p-value = 0.64). Adsorption of ammonia onto virgin PAC is thus considered immediate in the timeframe tested. An ANOVA defining PAC concentration, water temperature and initial ammonia concentration as independent variables was realized on the entire 0-d dataset. This analysis allowed us to conclude on the significance of the impact of PAC concentration, water temperature and initial ammonia concentration under the various operating conditions investigated. Overall, temperature impacted significantly ammonia removal as adsorption was increased at lower temperature (p-value < 0.01). In particular, the ANOVA highlighted that the impact of water temperature was significant in SW, while it was not in spiked SW (p-value < 0.01). Such result is coherent with thermodynamic data showing that the adsorption of basic molecules onto plant-based activated carbon is exothermic (Tan et al., 2008). When increasing the PAC concentration from 1 to 5 and then to 10 g L^{-1}, the behavior of the system does not appear monotonous. With a 1 g L^{-1} concentration, no significant ammonia removal was detected in SW and less than 10% was adsorbed in spiked SW. Using PAC concentrations of 5 or 10 g L^{-1}, ammonia removal increased from 43 to 48% in SW and from 64% to 73% (p-value < 0.01) in spiked SW. The slight difference between the removals obtained at 5 and 10 g L^{-1} demonstrates that, in this range of PAC concentrations, the availability of the adsorption sites is not a limiting factor under ambient ammonia concentration. In spiked SW, increasing the PAC concentration from 5 to 10 g L^{-1} led to less than a 10% increase in ammonia removal. This confirms the weak affinity of PAC for ammonia, attributable to the PAC physical and chemical characteristics (low surface acidity and pores of 10-20 Å) (Bandosz et al., 2009). Finally, even if the affinity of PAC for ammonia is not sufficient to reach a complete removal, the amount of ammonia adsorbed onto PAC in presence of NOM is not negligible, especially with PAC concentrations of at least 5 g L^{-1}. Modeling ammonia removal in a HMP should consequently account for adsorption especially under operating conditions favorable to this mechanism (i.e. high PAC concentrations and low PAC ages).

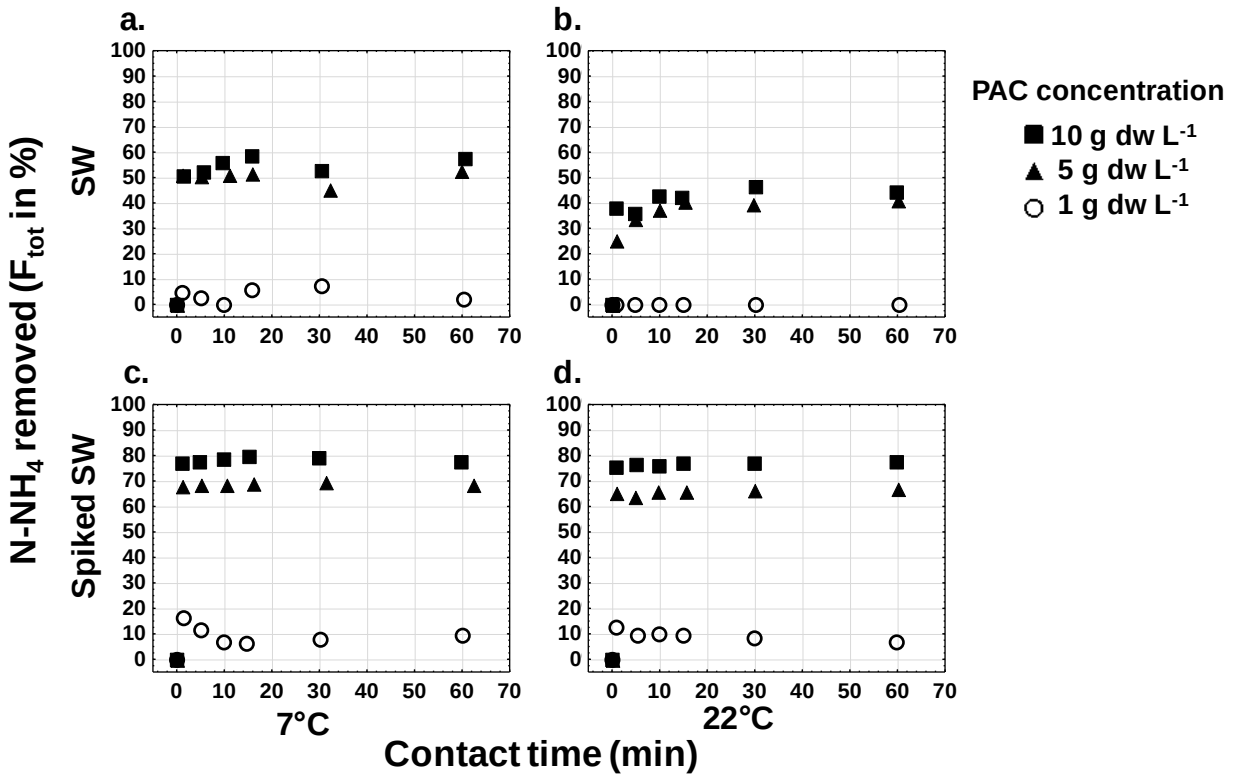

Figure 5-2 : Ammonia removal kinetics (F_{Tot} in %) on virgin PAC at 7°C (a, c) and 22°C (b, d) in SW (a, b, initial ammonia concentration is 62 ± 0 µg N-NH_4 L^{-1}) and spiked SW (c, d, initial ammonia concentration of 998 ± 13 µg N-NH_4 L^{-1}).

5.3.1.2 Ammonia removal on colonized PAC

5.3.1.2.1 Performance in settled water (SW)

Ammonia removal kinetics using 10-d or 60-d PAC at 7°C and 22°C are presented on Figure 5-3. Patterns observed (Figure 5-3) differ largely from those of virgin PAC (Figure 5-2). Both 10-d and 60-d PAC offered a nearly complete removal of ammonia at 22°C. In the following sections, results are discussed according to the main operating parameters investigated: PAC age, PAC concentration, and the HRT in the PAC contactor.

PAC age. Comparing Figures 5-3a and 5-3b with Figures 5-3c and 5-3d highlights the dissimilar kinetic behavior observed on 10-d and 60-d PAC. Nitrite and nitrate measurements (data not shown) confirmed that no nitrification was occurring at 7°C on 10-d PAC, while it contributed to achieve complete removal at 22°C. The slowing down of the nitrifying biomass activity with

lower temperature is consistent with previous observations in PAC contactors (Markarian et al., 2010; Suzuki et al., 1998) and in biological filters (Andersson et al., 2001; Kors et al., 1998; van der Aa et al., 2002). As no significant amount of ammonia was removed at 7°C in SW, the adsorption sites for ammonia at the surface of the 10-d PAC were assumed to be exhausted. As ammonia adsorption was demonstrated to be favored at 7°C (section 5.3.1.1.), one can infer that ammonia adsorption in SW onto the 10-d PAC at 22°C was negligible.

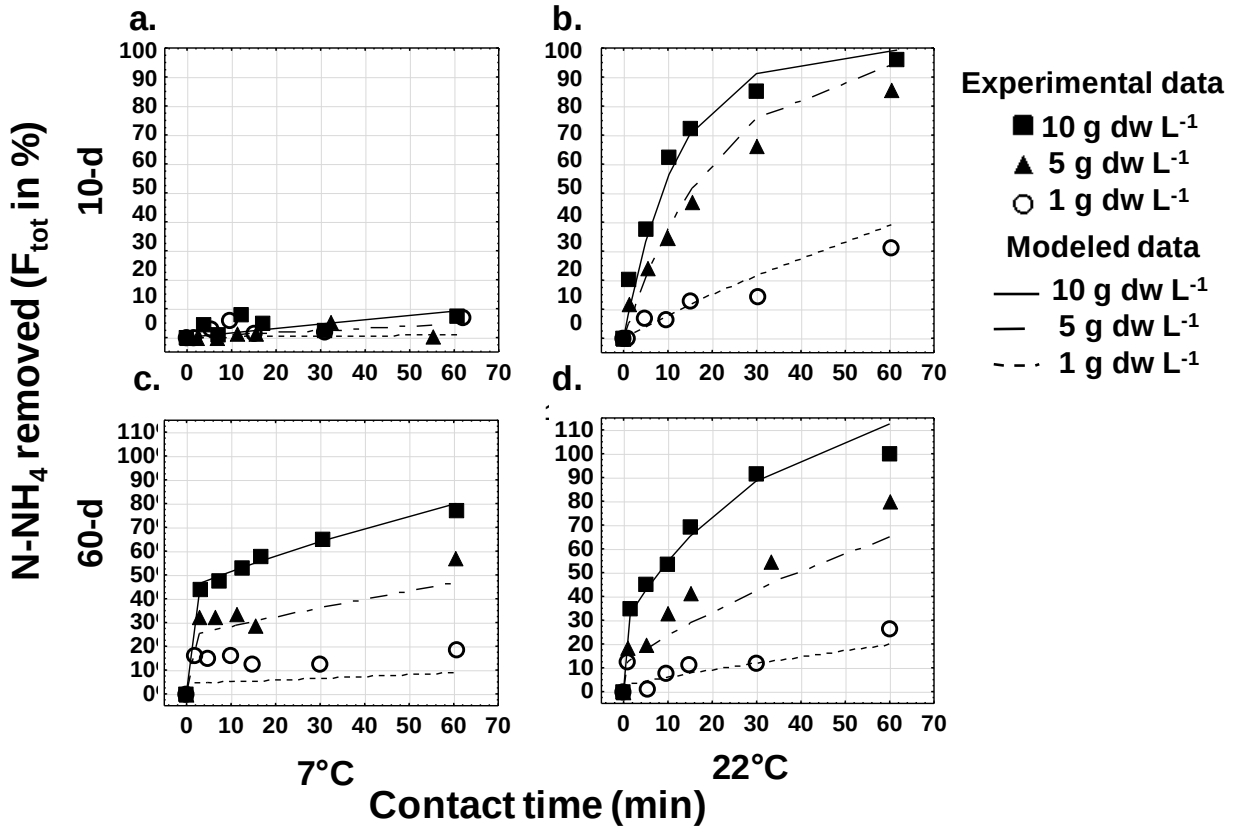

Figure 5-3 : F_{Tot} kinetics in SW (initial ammonia concentration is 91 ± 19 µg N-NH_4 L^{-1}) with PAC concentrations of approximately 1, 5 and 10 g L^{-1} at 7°C (a, c) and 22 °C (b, d) and with PAC age of 10-d (a, b) and 60-d (c, d). Experimental results correspond to the markers. Lines for 1 and 10 g L^{-1}correspond to modeled results and the 5 g L^{-1} is a prediction using the fitted parameters of 1 and 10 g L^{-1}.

For the 60-d PAC, following a temperature decrease from 22°C to 7°C, ammonia removal after 60-min decreased from 100% to 78 % at 10 g L^{-1}, from 80% to 58% at 5 g L^{-1} and from 25% to 18% at 1 g L^{-1}. At both temperatures, ammonia removal was characterized by a steep slope in the first minute, which is more pronounced at 7°C. This is characteristic of an adsorptive

phenomenon (section 5.3.1.1.). Ammonia was then removed at a lower rate for the remaining 59 minutes of contact time. This subsequent removal was favored at high temperature due to nitrification. Nitrite and nitrate measurements at 7°C (data not shown) confirmed that adsorption was accounting for a removal ranging from 10% to 25% at 7°C, while nitrification was responsible for the remaining removal (10-40%). Unlike on 10-d PAC, nitrifying bacteria remained partially active on 60-d PAC at 7°C. A residual adsorption capacity was also observed. This later result appears surprising as the adsorption capacity of PAC usually decreases with its age. However, the carbon contactor of a HMP does not only contain PAC, particularly when operated at high PAC ages. Indeed, the aged PAC suspension also accumulates suspended solids originating from the influent (SW). Léveillé et al. (2013) demonstrated that the reactor of the HMP pilot installed at the Ste Rose DWTP accumulated total suspended solids containing alum microflocs and nitrifying bacteria at a rate of 2 mg L^{-1} h^{-1}. We suggest that the presence of suspended solids favored the higher ammonia adsorption observed on the 60-d PAC. In summary complete ammonia removal is possible on both 10-d and 60-d PAC at 22°C. However, the PAC age appears to be a key operating parameter as maintaining a PAC age of 60-d gave the best overall ammonia removals with lower PAC dosages.

PAC concentration. At pilot-scale, both PAC contactors (10-d and 60-d) were colonized by nitrifiers such that complete ammonia removal was observed in the summertime (Léveillé et al., 2013). Due to technical constraints, both pilot-scale reactors were operated at different PAC concentrations: the 60-d PAC was colonized at 10 g L^{-1} and the 10-d PAC at 4 g L^{-1}. When discussing the importance of the PAC concentration on the efficiency of the process, these operating conditions must be kept in mind. For both PAC ages, almost complete ammonia removal was reached at lab-scale when applying the corresponding pilot-scale concentration (cf. Figures 5-3b and 5-3d). With 60-d PAC, the maximal removal was thus reached at 10 g L^{-1}. Assays realized at approximately 5 and 1 g L^{-1} using the same PAC led to lower removals because the nitrifying biomass was approximately divided by 2 and 10 during the laboratory tests. With a 10-d PAC (colonized at 4 g L^{-1}), the amount of nitrifying biomass required to oxidize the ambient ammonia in SW was present at the PAC surface (100% ammonia removal was observed at pilot scale at the time of sampling). Almost complete removal of ammonia (86%) was also observed at 5 g L^{-1} at lab-scale. The slight difference between the removal efficiencies can be explained by the small differences in the PAC concentrations applied and the

HRTs between lab- (60 min) and pilot-scale (67 min). Increasing artificially the concentration of nitrifying bacteria by raising the 10-d PAC concentration from 5 g L^{-1} to 10 g L^{-1} steepened the initial slope of ammonia removal, leading to an improved overall performance. In the colonizing conditions tested at pilot-scale, even the lower PAC concentration (4 g L^{-1}) operated at the lowest age (10-d) was sufficient to support the nitrifying biomass required to reach complete ammonia removal. Consequently, growth of nitrifying bacteria was not limited by the surface available for colonization on the PAC and/or suspended solids inside the contactor. As shown later, the same amount of nitrifying biomass was present in both reactors as the HRT required to reach the complete removal was the same. Since both reactors were fed with the same nutrient flux, the later is assumed to be the limiting factor for the growth of nitrifiers. In summary, PAC concentration does not appear to be a significant parameter for the removal of ammonia when nitrification is the dominant process and ammonia concentration is low.

Contact time (HRT). Even if ammonia adsorption on PAC is not negligible, we demonstrated that maintaining an optimized nitrification is crucial to achieve full removal. Increased contact time favored nitrification and allowed the higher process performance. For example, a 60-min contact time was required to reach a complete ammonia removal at the colonizing concentrations of both PACs. Such result is coherent with the fact that the pilots were also operated at an HRT close to 60 min. As suggested above, ammonia flux (set by the HRT) was most probably the limiting factor in the nitrifying biomass growth and thus in the ability of the process to reach complete ammonia removal.

5.3.1.2.2 Performance in spiked settled water

In spiked SW, initial ammonia concentration was increased about 10 times while the NOM concentration remained unmodified. The kinetics in spiked SW (Figure 5-4) thus provide additional information on the potential of the PAC contactor to face a sudden peak of ammonia. Removal kinetics were drastically affected by the spike (Figure 5-3 vs Figure 5-4). A steep initial slope, characteristic of ammonia adsorption, was noticed during the first minute for both 10-d and 60-d PACs at 7°C and 22°C. The second phase, characterized by a milder slope, reflected an important slowdown in ammonia removal. In this stressed condition, both PACs allowed maintaining a significant performance (30-50% removal depending on the operating conditions) thanks to a combination of adsorption and nitrification.

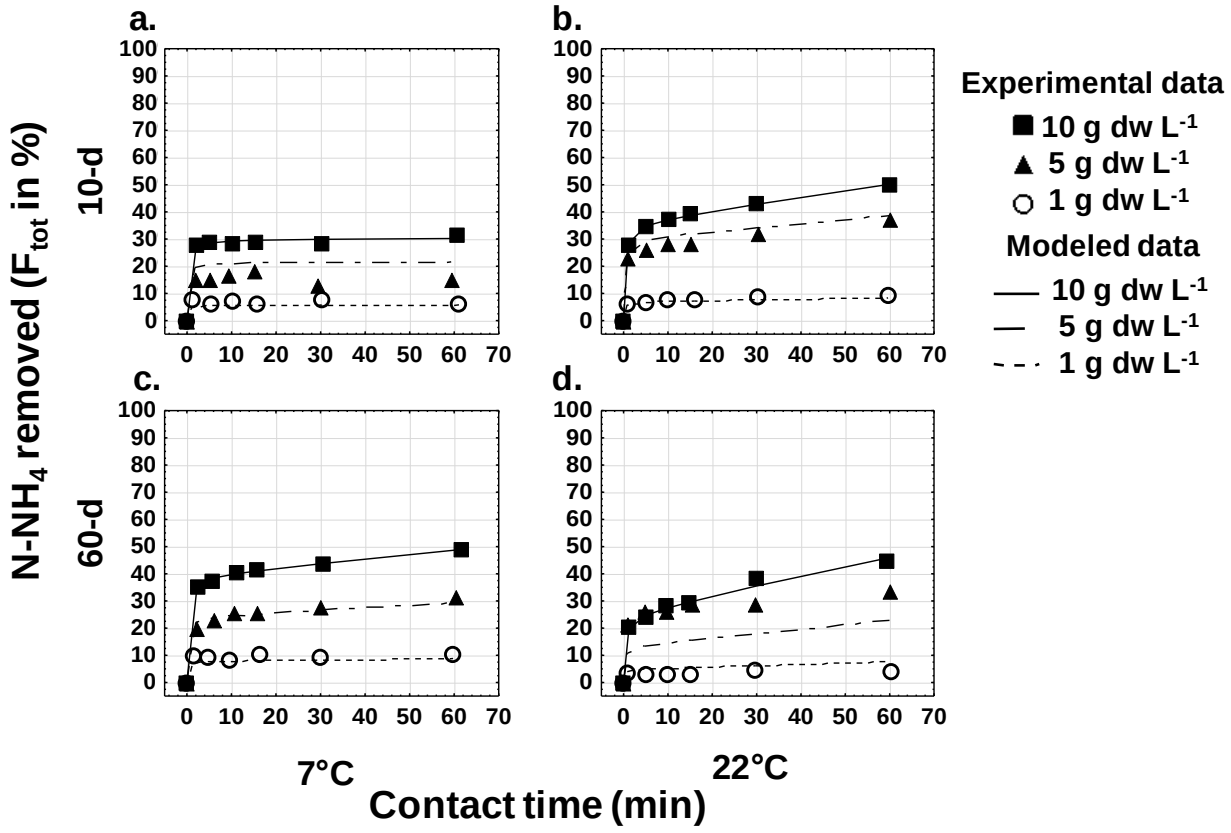

Figure 5-4 : F_{Tot} kinetics in spiked SW (initial ammonia concentration is 965 ± 61 µg N-NH_4 L^{-1}) with PAC concentrations of approximately 1, 5 and 10 g L^{-1} at 7°C (a, c) and 22 °C (b, d) and with PAC age of 10-d (a, b) and 60-d (c, d). Experimental results correspond to the markers. Lines for 1 and 10 g L^{-1}correspond to modeled results and the 5 g L^{-1} is a prediction using the fitted parameters of 1 and 10 g L^{-1}.

While almost no adsorption occurred on 10-d PAC in SW (see Figure 5-3a), nitrite and nitrate measurements completed at 7°C demonstrate that 6-28% of ammonia was adsorbed in spiked SW. Secondly, the importance of adsorption (i.e. removal during the first minute of contact time) was similar for both the 60-d PAC and the 10-d PAC. The results at 7°C in spiked SW thus highlight that the residual adsorption capacity is significant on both colonized PACs. By enhancing the mass transfer towards the surface of the PAC and suspended solids, the adsorption equilibrium established during the colonization of the PAC was therefore altered. As the amount of ammonia adsorbed on PAC depends on the relative concentrations of the other compounds in the water (Lebeau et al., 1999), spiking ammonia in the SW increased its competitiveness for the adsorption sites. However, nitrification kinetic was impacted in the opposite direction. Under

spiked ammonia condition, nitrification on the 60-d PAC at 7°C was responsible for less than 10% of the ammonia removal (even at 10 g L^{-1}) and was negligible on the 10-d PAC. At 22°C, nitrification occurred at a slower rate than expected. For example, doubling artificially the biomass from 5 to 10 g L^{-1} of 10-d PAC did not modify the nitrification rate observed after the fast initial adsorption step. Such result demonstrates a limitation of ammonia nitrification under spiked conditions. In a non-limiting environment, ammonia removal kinetic is expected to be maximal under such condition. Since assays performed under ambient and spiked conditions were run in parallel, the possibility of having different nitrifying populations on the PAC used to run the experiments can be rejected. On the other hand, dissolved oxygen and pH are factors typically responsible for losses of nitrifying activity. In this case, these assumptions were also discarded as i) dissolved oxygen was maintained at saturation due to mixing during the lab assays and ii) pH decrease due to ammonia oxidation was not sufficient to cause a decrease of the activity of the nitrifying bacterial biomass. Another possibility is a phosphorus limitation. Phosphate concentration in the SW at the Ste-Rose DWTP is known to be in the order of 10 µgP L^{-1} (Prévost, 1991) and low phosphate concentration was proven to negatively affect nitrifying biomass activity (de Vet et al., 2011; van der Aa et al., 2002). Studies agree that a phosphate concentration < 15 µgP L^{-1} would limit nitrification at ammonium concentration of 1 mg N L^{-1} and above, especially at low temperature (de Vet et al., 2011; Kors et al., 1998; van der Aa et al., 2002). Therefore, the limitation of the nitrifying biomass growth was probably switched from ammonia to phosphate availability when spiking SW with ammonia.

5.3.2 Modeling ammonia removal in a hybrid membrane process

As evidenced in section 5.3.1.2, the 10-d and 60-d PAC do not behave similarly in terms of adsorption. Removal kinetics are also affected by the spike of ammonia, which impacted adsorption and nitrification kinetic. Modeling is thus used as a tool to better understand these phenomena. In that context, fitting the entire dataset using the proposed model (cf. Eq. 5-10) did not fulfill our goal of describing accurately the kinetics measured at lab-scale with a a single set of parameters (i.e. R^2_a =0.44 for the entire dataset). As a consequence, the dataset was split in four groups according to PAC ages (10-d vs 60-d) and initial ammonia concentrations (ambient vs spiked). The model was used to simultaneously fit the experimental kinetics in 1 and 10 g L^{-1} reactors for these four groups. Data from the 5 g L^{-1} reactors were put aside for subsequent model

validation. As observed on Figures 5-3 and 5-4 (lines correspond to the modeled ammonia removals), this modeling strategy proved to be successful as the adjusted R^2 were found to be high (0.952-0.995) for all four data groups (cf. Table 5-2). The following sections will review and discuss the fitting parameters for adsorption and nitrification.

Table 5-2 : Values obtained for each parameter through non-linear estimations based on the 1 and 10 g L^{-1} data

Parameters		Description	Units	10-d SW		10-d Spiked SW		60-d SW		60-d Spiked SW	
				Mean value	Standard error	Mean value	Standard error	Mean value	Standard error	Mean value	Standard error
F_{nit}	A	Characterizes nitrifying biomass growth and density on the PAC	L g^{-1} s^{-1}	**5.2E-03**	**4.1E-04**	1.7E-04	9.6E-05	**2.2E-03**	**4.3E-04**	**3.2E-04**	**3.9E-05**
	Θ_{nit}	Arrhenius Law: Impact of temperature on nitrification	-	**1.3E+00**	**3.7E-02**	**1.3E+00**	**3.4E-01**	**1.1E+00**	**2.7E-02**	**1.0E+00**	**1.7E-02**
F_{ads}	K	Affinity of PAC for ammonia	µg g^{-1}(µg L^{-1})$^{-1/n}$	-	-	3.7E-05	4.2E-05	8.8E-02	6.2E+01	5.2E-04	6.2E-04
	n	Adsorption strength	-	-	-	**4.7E-01**	**3.6E-02**	1.3E+00	2.8E+02	**6.0E-01**	**6.7E-02**
	k_2	Velocity of ammonia adsorption	g µg^{-1} h^{-1}	-	-	**1.0E-01**	**2.4E-02**	5.5E+01	7.8E+02	1.8E-01	9.3E-02
	Θ_{ads}	Arrhenius Law: Impact of temperature on adsorption	-	-	-	**1.0E+00**	**1.9E-03**	9.5E-01	1.2E+00	**9.6E-01**	**4.2E-03**
R_a^2		R^2 adjusted (*)	-	0.973		0.995		0.952		0.991	

Bold values are significant

(*) R_a^2 is calculated as a function of the number of parameters (p) and the size of the sample (n)

Adsorption modeling. Experimental results demonstrated that adsorption was not negligible in spiked SW. Under ambient condition, nitrification only allowed describing accurately the 10-d results (R^2_a= 0.973) while it did not allow predicting accurately the 60-d PAC experimental dataset (R^2_a = 0.85; fit not shown). Therefore, for three out of four groups of data, the adsorption term in Eq. 5-10 was necessary to properly simulate the profiles of the experimental curves (cf. Figures 5-3c and 5-4c and 5-2d and 5-3d) (see Table 5-2). The adsorption modeling parameters included the Freundlich terms (K, n), a temperature coefficient (Θ_{ads}) as well as a kinetic term (k_2). The 60-d PAC results demonstrate that adsorption has to be taken into account in SW. However, all four adsorption parameters were not statistically significant (see Table 5-2). This observation suggests that the Freundlich and PSO kinetic models were not adequate to describe the behavior of ammonia adsorption under ambient condition. On the opposite, only the affinity constant (K) was not significant (p-value > 0.05) under spiked conditions. Values obtained for the adsorption-related parameters illustrate : i) the exothermicity of ammonia adsorption (Θ_{ads}-value

< 1); ii) the weak affinity of aged PAC for ammonia and iii) an adsorption capacity that varies greatly with the concentration of the compound in the bulk water (n-value ~ 0.5).

Nitrification modeling. The nitrification-related parameters were found to be significant for all four groups of data. The impact of water temperature on nitrification was corroborated by the fitted Θ_{nit}-values. The Θ_{nit}-value obtained for 60-d PAC (i.e. 1.07) corresponds to values referred to in the literature for nitrification in biological processes (i.e. 1.06-1.123 in Metcalf and Eddy Inc. (2003)). On the other hand, the Θ_{nit}-value for the 10-d PAC (i.e. 1.3) falls out of the range reported. This is in accordance with experimental observations, where negligible nitrification took place at 7°C on 10-d PAC while it was active on the 60-d PAC at 7°C. This behavior noticed at lab-scale is consistent with observations made two years in a row at the pilot-plant used for the colonization of the PAC used in the present study (Léveillé, 2011). However, the high Θ_{nit}-value obtained for the 10-d PAC is most likely due to an imprecise evaluation of the temperature effect for this condition as the absence of nitrification at 7°C makes the proper evaluation of the Θ_{nit}-value difficult.

The A-parameter characterizes both the nitrifying activity and quantity of biomass fixed onto the PAC. The growth term (cf. $\frac{\mu_{max}}{Y_S K_S}$) is expected to be the same for both aged PACs as both reactors were fed by the same influent under the same HRT. PNA measurements for both PACs are: $PNA_{10\text{-}d}$ =33.8±5.1 µgN h^{-1} g^{-1} and $PNA_{60\text{-}d}$ = 12.8±0.4 µgN h^{-1} g^{-1}. These values are comparable to published data for biological GAC filters: i) 10-20 µgN $g^{-1}\cdot h^{-1}$ in the first centimeters of a full-scale GAC filter treating water at moderate temperatures (i.e. 2.5-5 µgN $cm^{-3}\cdot h^{-1}$ using a conversion factor of 0.25 g of wet GAC per cm^3) (Andersson et al., 2001); ii) 56 µg N $g^{-1}\cdot h^{-1}$ as a maximum level after 146 days of operation at 20°C of a full-scale GAC biofilter (14 µgN cm^{-3} h^{-1} with 0.25 g cm^{-3}) (Kihn et al., 2002). They confirm that the biomass was approximately the same in both reactors as the ratio of the PNAs (i.e. $\frac{PNA_{10d}}{PNA_{60d}} \cong 2.6$) is comparable to that of the PAC concentrations in the reactors of the pilot-plant (i.e. $\frac{[PAC]_{60d}}{[PAC]_{10d}} \cong 2.8$). The difference between the A-values obtained in ambient condition ($A_{10\text{-}d}$=2.35 * $A_{60\text{-}d}$) is therefore attributed to different nitrifying biomass at the surface of both PACs. Under spiked conditions, as for the Θ_{nit}-values, the A-values were expected to remain identical to the ones in SW since the biomass did not have the time to adapt to the spike. However, the A-values decreased by an order of magnitude (Table

5-2). As discussed earlier, a phosphate limitation is the suspected cause of this decline in nitrification activity.

Model validation. Model validation was conducted by modeling the performance of the 5 g L^{-1} reactors using the developed models and the values of parameters originating from the 1 and 10 g L^{-1} datasets (see Table 5-2). Figures 5-3 and 5-4 illustrate that modeled removals for the 5 g L^{-1} reactors were good (i.e. modeling error is about 5%). In Figure 5-3d., an ammonia removal superior to 100% was achieved after 60 min when modeling a 10 g L^{-1} PAC concentration. This can be attributed to the model's structure (see Eq. 5-10), where the nitrified and adsorbed fractions are summed. To avoid such result, future modeling work should consider i) to sum the nitrification and adsorption rates instead of the removed fractions and ii) to enhance the description of ammonia adsorption equilibrium and kinetics.

Model predictions. Using the developed model, F_{Tot} were predicted for a reactor colonized at 5 g L^{-1} and HRT of 60 min under ammonia ambient condition. The values used for *A*-parameters were 5.2 x 10^{-3} L g^{-1} s^{-1} in SW and 1.7 x 10^{-4} L g^{-1} s^{-1} in spiked SW. Under this scenario, the respective contributions of biological activity and adsorption were calculated for the 10-d and 60-d PAC at 7 and 22°C. These results are presented Figure 5-5.

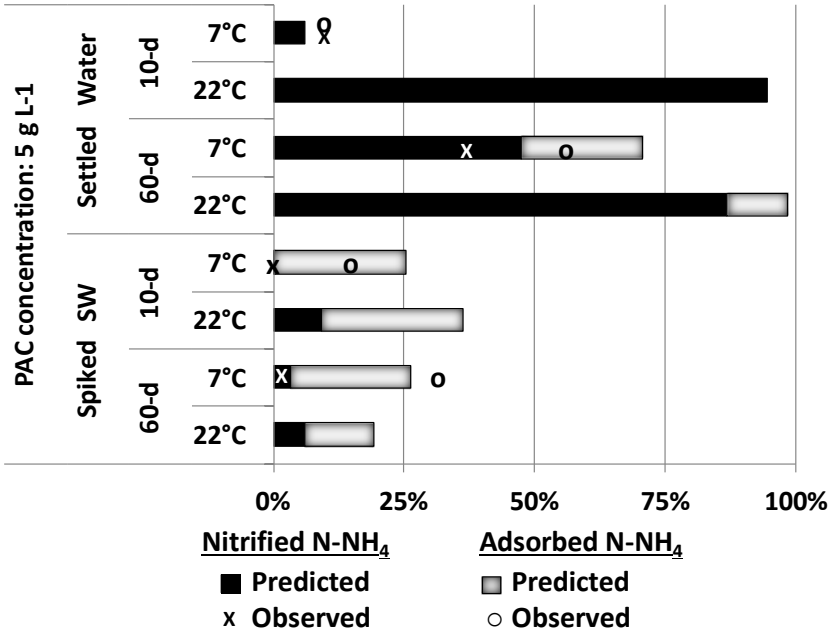

Figure 5-5 : Predicted and observed F_{Tot} (%) on 10-d and 60-d PAC, in SW and spiked SW (initial ammonia concentrations are 91 ± 19 µg N-NH_4 L^{-1} and 965 ± 61 µg N-NH_4 L^{-1},

respectively), at 7°C and 22°C at PAC concentration of 5 g L^{-1}. A 60-min contact time was applied. Black sections of the bar correspond to F_{Nit} and grey sections to F_{ads}. In SW, $A_{10\text{-}d} = A_{60\text{-}d} = 5.2 \times 10^{-3}$ L g^{-1} s^{-1} and in spiked SW, $A_{10\text{-}d} = A_{60\text{-}d} = 1.7 \times 10^{-4}$ L g^{-1} s^{-1}.

Under ambient ammonia condition, removal is mostly dominated by the role of nitrification. Nonetheless, at the lower temperature of 7°C, adsorption contributes significantly to the process and allows reaching higher ammonia removals than nitrification alone on 60-d PAC. The impact of temperature onto both mechanisms being opposite, the slowing down of bacterial activity is therefore partially balanced by an increased adsorption.

Under spiked ammonia condition, the contribution of nitrification was fairly low, probably due to phosphate limitation indirectly taken into account in the low *A*-values used. However, the gradient between ammonia concentration at the surface of the PAC and in the bulk water led to an increased ammonia adsorption. Adsorption allowed removing 13-27% of the ammonia and the 10-d PAC was predicted to be the most efficient. The potential of the PAC reactor of the HMP to face a sudden increase in ammonia concentration at the feed of the plant is thus mainly attributable to the increased contribution of adsorption. However, complete removal is not reached.

5.4 Discussion

On virgin PAC, ammonia adsorption was nearly immediate and exothermic. Adsorption was not negligible even in the presence of NOM as long as high PAC concentrations were used (i.e. at least 5 g L^{-1}) as observed by Ma et al. (2012). On colonized PAC, ammonia adsorption in SW was negligible on 10-d PAC but occurred when using 60-d PAC even though aged PACs were expected to be exhausted. Adsorption of ammonia onto the biofilm may partially explain these results (Nielsen, 1996). However, ammonia adsorption was observed on biofilms in activated sludge, which present more extended biofilms. More importantly, the 60-d PAC reactor includes as much as 1.6 g L^{-1} in total suspended solids, mostly composed of organic matter and residual alum micro-flocs (Léveillé et al., 2013). Adsorption on accumulated suspended solids is a probable cause considering that Bassin et al. (2011) indicated that adsorption of ammonium on suspended solids in activated sludge reactors and aerobic granular sludge reactors should be accounted for. In addition, residual adsorption capacity was demonstrated by exposing colonized PAC to spiked ammonia conditions. In our model, ammonia adsorption equations were

developed for one adsorbent only (activated carbon), i.e. without considering the potential impact of suspended solids. The poor performance of the Freundlich equation to describe ammonia adsorption is most probably the consequence of the presence of multiple adsorbents: the aged PAC and the suspended solids. Future work should therefore consider the potential role of these solids on overall process performance. The investigation of adsorption characteristics of various new and aged PAC regarding ammonia would also be of interest.

While significant ammonia adsorption can be achieved, nitrification remains the crucial mechanism to reach complete ammonia removal on colonized PAC. PAC age is thus an operating parameter of major importance as the nitrifying bacterial activity should be optimized. In this study, colonized PACs were representative of a full-scale PAC stabilized at a given retention time by a purge/dosage system. Among the ages tested, the 60-d PAC was more efficient than the 10-d PAC, especially at 7°C as the nitrifying activity on the 60-d PAC was still high, as observed on full-scale biological GAC filters at moderate temperatures (4-10°C) (Andersson et al., 2001). On the opposite, the 10-d PAC nitrifying activity was negligible at 7°C. Increasing the PAC age from 10-d to 60-d therefore enhances the ammonia removal in the HMP and divides the operational cost associated to PAC consumption by 6, as the PAC dosage is inversely proportional to the PAC age (Stoquart et al., 2012). Hu et al. (2014) observed that nitrifying bacteria growth on a 40-d period was favored at higher PAC concentrations. This could potentially explain the higher efficiency of the 60-d PAC. As illustrated Figure 5-1, the biofilm of a 60-d PAC is composed of a fraction of very large particle ages, which may reach as much as 400-d for a 60-d PAC and 60-d for a 10-d PAC. Since the age of the biofilm has been demonstrated to influence the composition of the bacterial communities, the bacterial population of a younger biofilm will differ from an older biofilm (Martiny et al., 2003). The increased sensitivity to water temperature of the 10-d PAC could be related to the differences in nitrifying populations on both PACs. This phenomenon is accentuated in the 10-d PAC reactor due to the heterogeneity of the PAC age distribution, which may include a large fraction of poorly colonized PAC (e.g. ages > 7d). A better understanding of both the bacterial population dynamics established in these biofilms and the temperature impact on these populations are however required to confirm this hypothesis.

Unlike PAC age, PAC concentration was not a key factor as biomass colonization was not limited by the surface available for bacterial growth but rather by the nutrient influx and water temperature. Therefore, a PAC concentration superior to 5 g L^{-1} would not appear profitable for

ammonia removal as complete removal was reached in the HMP under biological mode after 60 min in ambient condition at that concentration. Under a transient spike of ammonia, phosphate limitation was assumed to be responsible for the unexpectedly low amount of ammonia nitrified. If this hypothesis is confirmed, phosphate supplement might be an alternative to promote increased nitrification even at low temperature. Phosphate increase at the influent of filters allowed full restoration of nitrification even at 1°C (Kors et al., 1998). Alternatively, resilience to shock load was demonstrated to increase with high PAC concentrations (50-75 g L^{-1}) (Ma et al., 2012). Ma et al. (2013) reported ammonia removals as high as 90% at 10°C in a PAC-Membrane bioreactor system treating micro-polluted surface water. Finally, Kors et al. (1998) observed ammonia removing capacity in rapid sand filters increases within a few days. In the case of an extended exposition to high ammonia concentrations, efficiency of the PAC reactor is thus expected to increase due to the growth of nitrifiers.

Under warm water temperatures, the efficiency of the HMP for ammonia removal appears comparable to biological GAC filters. However, unlike biological filters, a significant adsorption capacity of colonized PAC was demonstrated for ammonia. In particular, model predictions highlighted a potential for ammonia adsorption to partially counteract the decrease of nitrifying activity in order to maintain a significant ammonia removal at low temperature or under a spike ammonia condition. In addition, the residual adsorption capacity of ammonia onto colonized PAC is of significance. A HMP reactor operated with colonized PAC should therefore be considered as a dual process able to remove dissolved contaminants such as micropollutants, ammonia and dissolved organic carbon through adsorption along with biodegradation. To improve the economic competitivity of the HMP process, reducing the HRT below 60 min is of interest. The capital expenditures would be significantly decreased and the increased nutrient load is expected to favor the installation of a larger biomass. However, the associated benefit of decreasing the HRT will be limited by the nitrifying kinetics (μ_{max}). Applying HRT-values closer to biological filters (e.g. 10-15 min) is probably a good HRT that would warrant further investigations. A subsequent study relating the impact of colonization conditions on process performance would then be required.

5.5 Conclusion

This study brings original data to better understand and optimize ammonia removal in the HMP. The following conclusions were drawn:

- Nitrification is the most important mechanism in order to reach a complete ammonia removal.
- Adsorption of ammonia should not be neglected and is required to properly model the performance of the HMP under all operating conditions.
- The sensitivity to water temperature is the weakness of the process as adsorption does not completely overcome the loss of nitrifying biomass activity at low temperature.
- The average PAC age and the nutrient load are key operating parameters. PAC age should be set high to favor nitrification. Since PAC dosage in inversely proportional to PAC age, increasing PAC age can also significantly lower the operating costs.
- The HMP operated with colonized PAC is expected to be as efficient as biological filters for ammonia removal.
- A significant ammonia adsorption capacity was evidenced on colonized PAC. This adsorption capacity is not fully exploited for ammonia removal. This demonstrates a great potential for the removal of other compounds (such as NOM and organic micropollutants), which are of major concern in the DW industry.

Future research should evaluate the efficiency of the HMP to remove biodegradable and non-biodegradable contaminants with colonized PAC.

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CHAPTER 6 ARTICLE 5 - DISSOLVED ORGANIC CARBON REMOVAL USING AGED POWDER ACTIVATED CARBON IN A HYBRID MEMBRANE PROCESS

This chapter is devoted to the investigation of dissolved organic carbon removal in the PAC contactor of an HMP. DOC, BDOC and RDOC removal kinetics were monitored on virgin and aged PACs under various operating conditions (temperature, PAC concentration, water matrix). Kinetics monitored on abiotic samples of the aged PACs and the impact of the water temperature on DOC/RDOC/BDOC removals allowed us to determine the extent of the biodegradation occurring on aged PAC under the conditions investigated. A kinetics model was developed to describe DOC removal in PAC contactors operated at steady-state with aged PAC. Its original feature was the integration of the PAC age distribution for predicting DOC removals. This chapter is a paper submitted to *Water Research*.

DISSOLVED ORGANIC CARBON REMOVAL USING AGED POWDER ACTIVATED CARBON IN A HYBRID MEMBRANE PROCESS

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ABSTRACT

Hybrid membrane processes (HMPs) couple powder activated carbon (PAC) with low-pressure membrane filtration. In this study, DOC removal achieved using an aged (10-d and 60-d) PAC suspension (1 to 10 g L^{-1}) was investigated. As aged PACs were shown to be colonized by heterotrophic biomass, the focus was placed on discriminating the mechanisms responsible for DOC removal: biodegradation and/or adsorption. DOC, biodegradable DOC and refractory DOC removal kinetics occurring in the carbon contactor were characterized at lab scale under varying conditions (temperature, PAC concentration, PAC age and water matrix). DOC biodegradation contributed marginally to DOC removal in the investigated conditions. An original model integrating the PAC age distribution was developed to describe DOC removal in PAC contactors operated at steady-state and a high PAC age. At a mean PAC residence time of 60 d, the less aged PAC fraction (25 d and less) was primarily responsible for DOC adsorption (> 80%). This fraction represents 34% of the mass of PAC present in the contactor. When using a water matrix with a higher initial DOC concentration or a lower affinity to PAC, the residual adsorption capacity of that older fraction was demonstrated to be useful.

KEYWORDS

Hybrid membrane process - DOC adsorption – Modeling – PAC - Drinking water

6.1 Introduction

The removal of natural organic matter (NOM) is a central objective of drinking water treatment using surface waters. Removing NOM reduces the chlorine demand at the final disinfection stage and the formation of chlorinated disinfection byproducts such as trihalomethanes, which have been subjected to stricter international legislation in recent decades. Removing the biodegradable fraction of NOM also minimizes the extent of microbial regrowth in drinking water distribution systems. Hybrid membrane processes (HMPs) couple the use of powder activated carbon (PAC) with low-pressure membrane filtration. As suggested by the rising number of publications on this topic, HMP offers a promising option to achieve high levels of dissolved organic carbon (DOC) and biodegradable DOC (BDOC) removal in addition to the removal of particulate contaminants, including protozoan parasites, such as *Cryptosporidium*. Average DOC removals reported in the

literature vary from 20% to 100%, depending on the operating conditions (Stoquart et al., 2012). HMP is also becoming a process of interest for the removal of trace organic micropollutants such as atrazine (Lebeau et al., 1998), hormones (Song et al., 2009), pharmaceuticals (Saravia et al., 2008) and microcystin (Campinas et al., 2010b). The available HMP studies have mainly been conducted at the pilot scale. Treatment performance has been shown to be impacted by factors such as i) PAC residence time (Léveillé et al., 2013; Markarian et al., 2010; Suzuki et al., 1998; Treguer et al., 2008), ii) PAC concentration and/or dosage (Kim et al., 2007; Markarian et al., 2010) and (iii) PAC size (Markarian et al., 2010). However, a strategy for identifying the optimal operating parameters has not been proposed yet. Most studies have operated HMPs in warm-water conditions with a low PAC age (i.e., 7 d or less) and relatively high PAC dosages (i.e., 10-200 mg L^{-1}). Considering seasonal fluctuations in water quality and potentially variable targeted performances, it is desirable to develop a modeling approach enabling the optimization of key operating parameters in the carbon contactor such as the PAC concentration or the PAC residence time, often referred to as PAC age.

The mechanisms responsible for DOC removal in PAC contactors are adsorption and/or biodegradation, both of which appear to be influenced by water temperature. To the best of our knowledge, no published study has sought to describe the mechanisms responsible for the performance of PAC contactors in NOM removal, yet such a description would allow the process to be optimized. However, the successful completion of such a study is challenged by the need to model both mechanisms in parallel (adsorption and biodegradation). Similar to a biological GAC filter, aged PAC supports an abundant heterotrophic and nitrifying biomass (Stoquart et al., 2014a; Stoquart et al., 2014b). However, the complete adsorption capacity is most likely not exhausted in aged PAC. This situation raises the following questions: Is there any residual adsorption capacity in colonized PAC? To what extent do residual adsorption and biodegradation contribute to DOC removal?

The main objective of this study was to understand and describe the mechanisms responsible for DOC removal on aged PAC (> 7 d). In particular, an emphasis was placed on determining the respective contributions of adsorption and biodegradation to DOC removal in the carbon contactor of an HMP operated at high PAC age (i.e., 10 d and 60 d). More specifically, the DOC removal kinetics were characterized under various operating conditions; the impact of temperature, water matrix, PAC age and concentration in the contactor were investigated over a

broad range of operating conditions. DOC adsorption and biodegradation were discriminated by comparing removal kinetics with an abiotic control (i.e., colonized PAC exposed to gamma irradiation (Stoquart et al., 2013)). Finally, DOC removal in the PAC contactor of an HMP operated at steady-state and a high PAC age was modeled. Such information will enable the optimization of PAC usage and the reduction of operating costs.

6.2 Materials and Methods

6.2.1 Powder activated carbon aging

A meso- to macroporous PAC (wood-based Picahydro LP39, median diameter 15-35 µm) was chosen to favor bacterial biomass colonization. The PAC was aged in two industrial HMP pilot facilities where ultrafiltration membranes were immersed in a concentrated PAC suspension (as per Léveillé et al. (2013)). A stable mean PAC age in the carbon contactors was maintained by daily purging and replacing a fraction of the PAC. Thus, the PAC ages referred to herein correspond to the mean PAC residence time of a PAC age distribution in the sampled suspension. The targeted operating conditions were as follows: 10-d PAC at 4 g L^{-1} (3.5±1.2 g L^{-1}) and 60-d PAC at 10 g L^{-1} (9.8±1.1 g L^{-1}). The selected PAC ages allowed colonization of the PAC by heterotrophic and autotrophic nitrifying bacteria (Stoquart et al., 2014a). The HMP contactors were fed with alum-settled water from the Ste-Rose drinking water treatment plant (DWTP) (Laval, Qc, Canada) (pH = 6.70±0.11; turbidity = 0.62±0.40 NTU; UV_{254} = 0.056±0.007 cm^{-1}; DOC = 3.02±0.30 mg C L^{-1}; BDOC=0.27±0.11 mg C L^{-1}, alkalinity = 20±2 mg $CaCO_3$ L^{-1}) and operated with a 67 min hydraulic retention time (HRT).

6.2.2 Lab-scale kinetic study

Unlike in most studies, DOC, BDOC and refractory DOC (RDOC) removal kinetics were monitored in this study to discriminate DOC adsorption from biodegradation. Suspensions of (i) aged PAC and (ii) neutralized virgin PAC (exposed to 1 M NaOH solution 12-24 hours before the assays) were used. Aged and virgin PAC suspensions were filtered on 20-µm paper filter (Grade 41, Whatman®) to recover a dense PAC cake. Dry weights were evaluated in triplicate (2540-B technique (American Public Health Association (APHA) et al., 2012)). A portion of the PAC cake was resuspended in non-ozonated and pre-ozonated (pre-O_3) raw water (RW) or settled water (SW) from the Ste-Rose DWTP to achieve the targeted PAC concentration in 2-L reactors

(1, 5 or 10 g L^{-1}, dw). Removal values were also monitored on irradiated aged PAC. The dose of gamma rays applied (13 kGy) was optimized to inhibit the biomass activity without affecting the adsorption characteristics of the PAC (as per Stoquart et al. (2013)). The irradiated PAC was used as an abiotic control for DOC removal on aged PAC. Experiments conducted at a given temperature were always performed with PAC acclimated to that same temperature at the pilot plant. PAC concentrations are always expressed as dry weights (dw) herein. The operating conditions tested are summarized in Table 6-1.

Table 6-1 : Operating conditions tested

Water type	Settled water (SW)			Raw water (RW)	
Ozone dose (g O_3 g C^{-1})	0	0.8 ± 0.1	1.4 ± 0.1	0	0.7 ± 0.1
Initial DOC concentration (mg C L^{-1})	3.20 ± 0.41	3.05 ± 0.40	3.08 ± 0.35	7.17 ± 0.40	6.28 ± 0.53
Initial BDOC concentration (mg C L^{-1})	0.30 ± 0.11	0.64 ± 0.14	0.98 ± 0.09	0.45 ± 0.12	1.60 ± 0.23
Initial RDOC concentration (mg C L^{-1})	2.0 ± 0.44	2.42 ± 0.31	2.10 ± 0.32	6.72 ± 0.43	4.67 ± 0.41
Temperature (C)		7 ± 1 22 ± 1		7 ± 1	
PAC age (d)			0 10 60		
PAC concentration (g L^{-1})			1.0 ± 0.1 (*) 5.0 ± 0.8 9.7 ± 1.2 (*,**)		

Note: Irradiated PAC kinetics were monitores at 7 C in SW and pre-O_3 SW (*) and in RW and pre-O_3 RW (**)

The DOC, BDOC and RDOC concentrations were monitored over 60 min by sampling 125 mL of the 2-L PAC suspension at increasing contact times (1, 5, 10, 15, 30 and 60 min, 60 minutes being the highest contact time considered realistic for full-scale HMP operation). Samples were submitted to sequential filtration on a 1.5-µm microfiber glass filter (934-AH, Whatman®) followed by a 0.45-µm PES filter (Pall Supor®-450) to ensure the immediate separation of the PAC. Both filters had been previously rinsed with 1 L of Milli-Q water. The DOC concentration was measured with a TOC meter (Sievers 5310 C). BDOC analysis was completed using the method adapted from Servais et al. (1989) (as per Markarian et al. (2010)). RDOC concentrations were calculated by subtracting the BDOC from the DOC values (in mg C L^{-1}). All measurements were performed in triplicate. The detection limit of the method is 0.08 mg C L^{-1} for DOC and 0.11 mg C L^{-1} for BDOC and RDOC.

6.3 Results

6.3.1 NOM adsorption on virgin PAC

Assays on virgin PAC provide a control or reference for evaluating i) the potential maximum carbon removal achievable by adsorption in the conditions tested and ii) the impact of various operating parameters (contact time, temperature, water matrix and PAC concentration) on DOC, BDOC and RDOC adsorption.

A repeated measures ANOVA design (Statsoft, v11.0, USA) demonstrated that the contact time significantly impacted the DOC adsorption (p-value < 0.01). However, the majority of DOC was adsorbed within the first minute. As an example, in SW at 22°C, DOC removal using 4.5 g L^{-1} reached 78% after the first minute and 85% after 60 minutes, which was also the maximal removal observed on 0-d PAC. The same statistical analysis also demonstrated that the impact of contact time was further minimized when using higher PAC concentrations (p-value < 0.01). Although statistically significant, the impact of contact time on DOC adsorption by 0-d PAC is thus considered marginal. The impact of the various parameters on DOC removal in SW are presented as boxplots in Figure 6-1, which include the varying DOC removals measured over 60 min. A similar figure using an RW matrix at 7°C was built and is presented in the Supplemental information (Figure A-3. 1).

6.3.1.1 Temperature

DOC, BDOC and RDOC removal increased at higher temperature (Figure 6-1). This behavior has been reported several times previously (Schreiber et al., 2005; Summers et al., 1988). The mechanisms responsible for this increase in efficiency with temperature are not entirely known. A credible explanation was proposed by Schreiber et al. (2005). Higher temperature reduces the adsorption of water molecules (Dabrowski et al., 2005) and therefore increases the hydrophobicity of the activated carbon. Thus, NOM adsorption is increased due to low competition for the adsorption sites at a high PAC concentration and temperature, which allows the aromatic NOM molecules to orientate in a flat configuration on the PAC, leading to electrophobic π-π interactions.

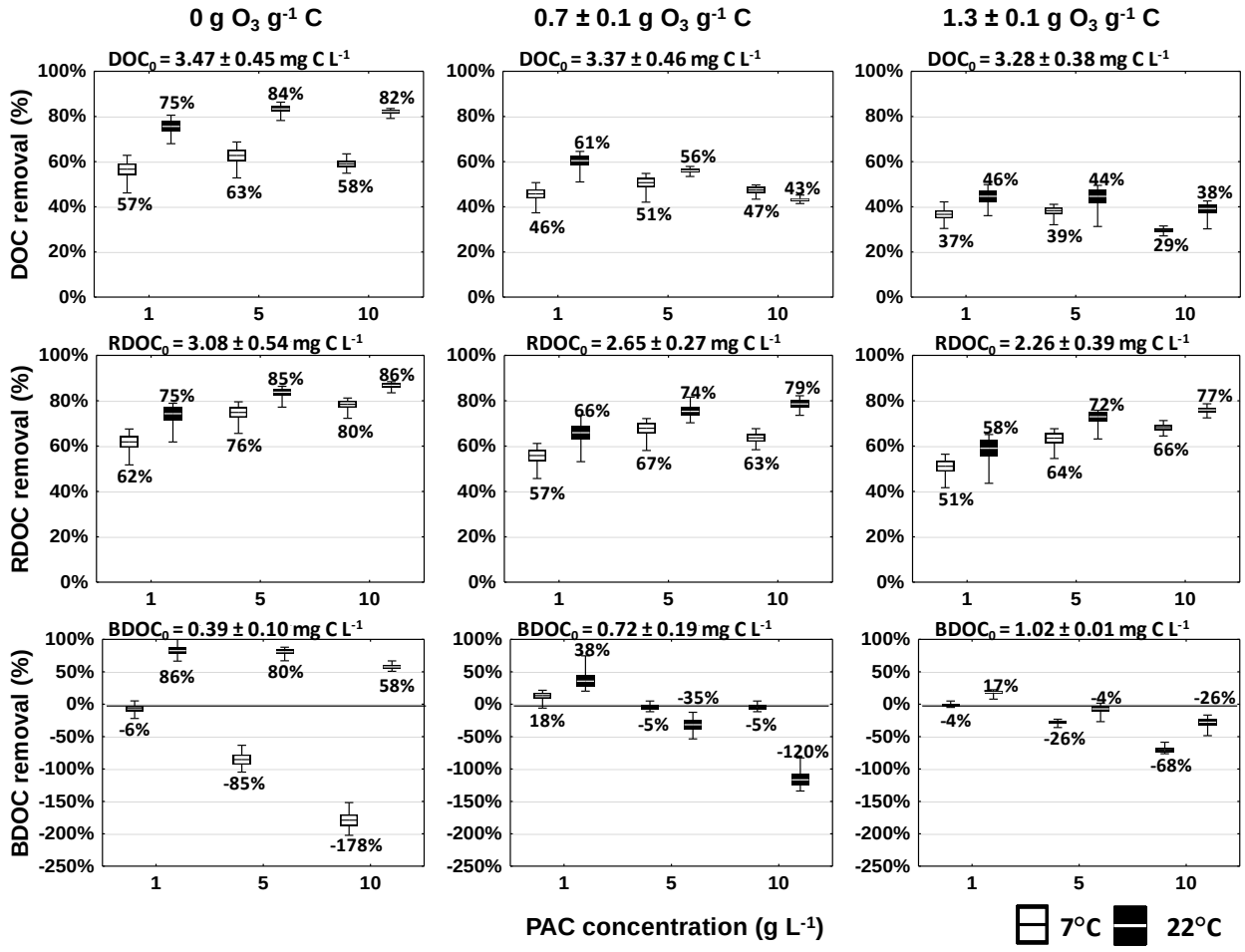

Figure 6-1 : DOC, BDOC and RDOC removals (in %, initial concentration presented above each graph) on virgin PAC at 7°C and 22°C. The PAC concentrations were approximately 1, 5 and 10 g L^{-1}, and the water matrices were SW (0 g O_3 g^{-1} C) and pre-O_3 SW (0.7 and 1.3 g O_3 g^{-1} C). The boxes represent the mean removal ± the standard error, and the whiskers correspond to the minimal and maximal removals.

6.3.1.2 PAC concentration

The maximal observed DOC removals at 7°C were 57% in RW and 69% in SW. At 22°C, the maximal observed DOC removal was 85% in SW. Surprisingly, the overall DOC removal was not raised by higher PAC concentrations (see Figure 6-1, p-value = 0.20). RDOC removal (due to adsorption only) increased with PAC concentration in SW, especially when raising the PAC concentration from 1 to 5 g L^{-1} (Figure 6-1, p-value < 0.05). In contrast, there was no benefit in choosing a concentration of 10 g L^{-1} over 5 g L^{-1} (the difference in RDOC removal was only 2%

on average in SW). The release of BDOC from the PAC is the suspected cause for the lack of improvement with increasing PAC concentration. A net negative balance of BDOC adsorption and release is noticeable at high PAC concentrations (5 g L^{-1} and up) at 7°C in SW (Figure 6-1) and was evaluated as 0.04 ± 0.02 mg C g PAC^{-1}. At 22°C, the net balance was positive. The BDOC, RDOC and DOC removal percentages were similar (i.e., DOC = 80±5%, BDOC = 74±14%, RDOC = 82±7%). Similar removal percentages of DOC, BDOC and RDOC have been reported at the very beginning of the colonization of granular activated carbon filters (Servais et al., 1994). It is therefore suggested that in the absence of noticeable DOC release, DOC, RDOC and BDOC in SW are adsorbed similarly. At 7°C, we suggest that 85% was the maximal removal reachable by the virgin PAC at 10 g L^{-1}, as the net release evidenced under these conditions approximately corresponds to 15% of the initial DOC concentration.

To the best of our knowledge, BDOC release from wood-based PAC has never been reported before. As PAC is mostly used at low dosages, the corresponding BDOC releases are therefore undetectable. In an HMP, applying 10 g L^{-1} of PAC with an age distribution of 60 d and a 30 min HRT would require a PAC dosage of 3.5 mg L^{-1}, corresponding to a 0.15 µg C L^{-1} BDOC release. The extent of the DOC release should vary by carbon type and temperature. However, the released amounts are small and should therefore not be a concern for the water industry.

6.3.1.3 Water matrix pre-ozonation

Figure 6-1 illustrates the decrease in DOC removal due to pre-ozonation of the water matrix (p-value < 0.01). In SW at 22°C, the mean DOC adsorption was reduced from 80% to 53% with a dosage of 0.7 g O_3 g^{-1} C and to 43% with a dosage of 1.3 g O_3 g^{-1} C. In a pre-ozonated matrix, the impact of water temperature on DOC adsorption was no longer significant. The mean RDOC removal decreased from of 77% to 68% (with 0.7 g O_3 g^{-1} C) and to 65% (with 1.3 g O_3 g^{-1} C) (p-value < 0.01). The ozonation of NOM can lead to the formation of smaller hydrophilic (i.e., polar) and biodegradable molecules by breaking the aromatic rings of NOM (De Laat et al., 1991). Although smaller molecules diffuse better into porous structures, these newly formed molecules at ozone doses superior to 0.3 g O_3 g^{-1} C are typically less adsorbable (De Laat et al., 1991; Treguer et al., 2010). Therefore, the adsorption efficiency is reduced, and increasing the water temperature no longer favors DOC adsorption. BDOC release was not observed in 0.7 g O_3 g^{-1} C SW, and the BDOC release in SW pre-ozonated to 1.3 g O_3 g^{-1} C was similar to that in SW

(0.04 mg C g^{-1}). Thus, BDOC release is not only dependent on PAC dosage but also on the background water matrix.

6.3.2 Water matrix

Mean removal percentages cannot be directly compared between SW and RW, as the contact time significantly impacted NOM adsorption in RW (the DOC removal percentage was doubled between 1 and 60 minutes of contact time). Therefore, the percentages compared are the efficiency after 60 minutes and not the equilibrium capacities. Similar responses to the effects of PAC concentration and pre-ozonation were obtained in SW and RW at 7°C (see Figure A-3. 1 in the supplemental information). Performances measured after 60 minutes of contact with 11.1 ± 0.5 g PAC L^{-1} at 7°C were 53% in SW and 67% in RW. These percentages correspond to removals of 1.7 mg C L^{-1} in SW and 4.8 mg C L^{-1} in RW.

6.3.3 NOM removal on colonized PAC

In this section, general observations of DOC, BDOC and RDOC removals under various operating conditions are presented first. The respective contributions of DOC adsorption and biodegradation by colonized PAC will then be evaluated. Finally, the DOC removal kinetics in the HMP contactor will be modeled to propose a methodology to predict NOM removal in the carbon contactor of an HMP operated at a high PAC residence time.

6.3.3.1 DOC removal performance

The impact of contact time, PAC age, PAC concentration, temperature and water matrix (pre-O_3 and non-O_3 SW and RW) was evaluated by conducting kinetic lab studies equivalent to those presented for virgin PAC. Figure 6-2 illustrates the effect of the PAC age and ozone dose on the efficiency of the process in SW at 22°C. DOC, BDOC and RDOC removal kinetics (in %) are presented only for one PAC concentration (10.0 ± 0.5 g L^{-1}). Additional figures (Figure A-3. 2 and Figure A-3. 3) are provided as supplemental information. Figure A-3. 2 presents DOC, BDOC and RDOC removal kinetics (in %) at 3 PAC concentrations (approximately 1, 5 and 10 g L^{-1}) on 10-d and 60-d PAC. Figure A-3. 3 presents DOC removals (in %) at the same 3 PAC concentrations, on 3 PAC ages (0-d, 10-d and 60-d). The overall impact of the various operating parameters is presented in the following paragraphs. In general, DOC was never completely

removed from the SW. The highest removal was 49% when using 10-d PAC in SW at 22°C. The lowest performance was 12% removal, reached with 60-d PAC in pre-O_3 SW at 7°C.

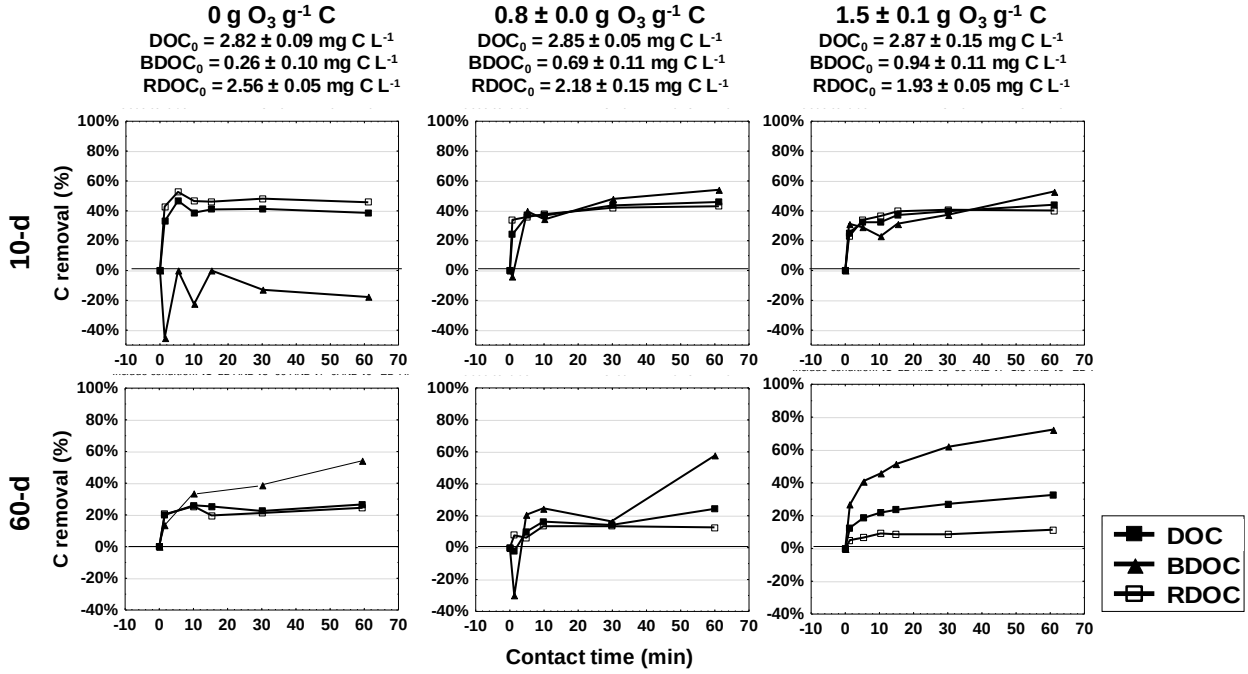

Figure 6-2 : DOC, BDOC and RDOC removal (in %) on 10-d and 60-d PAC at 22°C. SW was pre-ozonated at doses of 0, 0.8 and 1.5 g O_3 g^{-1} C. The PAC concentration was 10.0 ± 0.6 mg C L^{-1}.

6.3.3.1.1 Contact time

For most of the conditions tested, DOC and RDOC removal profiles (in %) were almost identical (see Figure 6-2 and Figure A-3. 2). In particular, DOC and RDOC curves both include an initial rapid removal (steep slope for the first minutes of contact time), followed by a milder removal rate for the remaining contact time. The impact of the contact time on DOC, BDOC and RDOC removal was always significant (repeated measure analysis of variance, p-value < 0.01). As for 0-d PAC, most of the DOC and RDOC removal occurred during the first minutes of contact time in SW (Figure 6-2, Figure A-3. 2 and Figure A-3. 3). The precision of the BDOC removal profiles was weak due to the low initial BDOC concentration in SW ($BDOC_0$ = 0.3±0.11 mg C L^{-1}, see Table 6-1). The initial BDOC concentration was increased in pre-O_3 water matrices. BDOC removal percentages in pre-O_3 water were similar to DOC and RDOC profiles when using 10-d

PAC, but superior when using 60-d PAC (p-value < 0.01, see Figure 6-2). This suggests active DOC biodegradation on 60-d PAC.

6.3.3.1.2 Temperature

DOC and RDOC removals were significantly increased at 22°C (p-value < 0.01), while BDOC removal was not significantly affected by the water temperature (p-value > 0.05). The impact of water temperature on process efficiency is depicted as supplemental information in Figure A-3. 2.

6.3.3.1.3 PAC concentration

As evidenced in Figure A-3. 2 and Figure A-3. 3, the PAC concentration significantly impacts DOC removal (SW: p-value = 0.03 and RW: p-value < 0.01). Differences in SW were marginal (0.2 mg C L^{-1}). In RW, the mean DOC removal increased from 25% to 35% (additional removal of 0.7 mg C L^{-1}) when raising the PAC concentration from 1 to 5 g L^{-1}. A 4% increase was gained by raising the PAC concentration to 10 g L^{-1} (additional removal of 0.3 mg C L^{-1}). Because the RDOC and DOC removal presented similar profiles, changes in the DOC removal performance can be attributed to changes in RDOC removal. The greater impact of the PAC concentration observed in RW is attributed to i) an increased initial DOC concentration and/or ii) a greater affinity of NOM for the PAC ($SUVA_{RW}$ = 3.3 > $SUVA_{SW}$ = 1.8); however, in SW, the availability of adsorption sites does not appear to be a key operating parameter in the range of concentrations tested.

6.3.3.1.4 PAC age

Figure 6-2 illustrates the decrease in process performance as PAC age increases (p-value < 0.01). The main loss of performance occurs when moving from 0-d to colonized PAC (10-d) (Figure A-3. 3). A further decrease in DOC removal occurred when raising the PAC age to 60 d (Figure 6-2 and Figure A-3. 3). With a value of 10.0 ± 0.6 g L^{-1} in SW, the mean DOC removal was reduced from 40% to 22% when raising the PAC age from 10 d to 60 d (Figure 6-2). RDOC removal followed the same trend (p-value < 0.01), while BDOC removal was not significantly impacted (p-value = 0.66).

6.3.3.1.5 Pre-ozonation of the water matrix

On 10-d PAC, pre-O_3 had a negative impact on DOC and RDOC removal (p-value < 0.01), while BDOC removal was not significantly affected (p-value = 0.24). Generally, the impact of pre-O_3 on DOC removal when using the 60-d PAC was not as important as for the 10-d PAC (see Figure 6-2). BDOC removal profiles were also higher than those for DOC (see Figure 6-2). This could be related to an increase in BDOC removal due to increased biodegradation activity with older PAC.

6.3.3.1.6 Water matrix

Using RW as the water matrix increased the initial DOC and altered the type of NOM to which the PAC is exposed, especially considering that the PAC aging process was always completed using SW. As previously mentioned, increased DOC removals were related to increased PAC concentrations in RW but not in SW (p-value <0.01). A similar analysis also demonstrated that the negative impact of using older PAC to remove DOC was less important in RW than in SW (p-value < 0.01). The increased initial DOC concentration, along with the fact that the 10-d and 60-d PAC materials were aged in SW, justify these results. This aspect is discussed later.

6.3.4 Modeling of DOC removal

6.3.4.1 Is biodegradation worth consideration?

Given that a significant amount of heterotrophic bacterial biomass was measured on 10-d and 60-d PAC (Stoquart et al., 2014a), biodegradation occurred on 10-d and 60-d PAC. Biodegradation is therefore a mechanism responsible for the depletion in DOC concentrations observed during the kinetic studies presented. Evidence of biomass activity includes i) the positive interaction between the age of the PAC and the contact time for BDOC removal on colonized PAC (p-value < 0.01); ii) the positive impact of water temperature on DOC removal (p-value < 0.01); and iii) the observation of higher BDOC removal profiles than DOC removal profiles when the BDOC and RDOC adsorption profiles were expected to be the same (cf. section 3.2.1, (Servais et al., 1994)). This last observation was found mostly in pre-O_3 SW at 22°C (see Figure 6-2), conditions which are the most favorable for biodegradation. The overall importance of biodegradation on process performance is however questionable. The relative importance of biodegradation and adsorption for DOC removal is discussed hereafter.

First, the initial BDOC concentration in SW corresponds to less than 10% of the total DOC content in SW (0.3 ± 0.1 mg C L^{-1}). In the best-case scenario, biodegradation in SW will be responsible for a maximum DOC removal of 10%. Based on DOC removal percentages obtained on 10-d and 60-d PAC (section 3.2.1), biodegradation was not the major mechanism contributing to DOC removal in SW. Hence, kinetics were monitored in pre-O_3 SW, as well as in RW and pre-O_3 RW, with the objective of placing the colonized PAC in contact with higher amounts of BDOC to emphasize biodegradation. In most of the operating conditions tested, the profiles obtained for DOC and RDOC removal remained similar (see Figure 6-2 and Figure A-3. 2), suggesting that BDOC removal also follows a similar profile. It appears that BDOC removal is therefore attributed to adsorption, as is RDOC. In the conditions most favorable for biodegradation (Figure 6-2, 22°C in pre-O_3 SW at a dose of 1.4 g O_3 g^{-1} C), the BDOC removal profile is superior to the profiles of DOC and RDOC, and biodegradation is therefore occurring. However, the contribution of BDOC removal only accounted for 20% of the entire DOC removal efficiency, a performance that cannot be entirely attributed to biodegradation, as BDOC can also be adsorbed. The contribution of biodegradation to DOC removal is therefore assumed to be of secondary importance.

Comparing BDOC removals on abiotic controls and colonized PACs confirms the marginality of the contribution of biodegradation to DOC removal at 7°C. Figure 6-3 illustrates that BDOC removal on colonized PAC was not significantly impacted by gamma irradiation (p-value = 0.86). The major difference observed in SW on 60-d PAC is attributed to a net BDOC release from the irradiated 60-d PAC rather than by an increase in BDOC removal due to biodegradation. Perturbation of the PAC sample due to transport for irradiation is the suspected cause of this release. It is thus concluded that at 7°C, DOC is removed by adsorption on 10-d and 60-d PAC.

As mentioned in section 3.2.1, DOC removal on colonized PAC was significantly increased when working at 22°C (p-value < 0.01). As a higher temperature is expected to favor higher BDOC removal through biodegradation, it was of interest to confirm whether this improved DOC removal was caused by improved bacterial activity. In SW and pre-O_3 SW (0.8 g O_3 g^{-1} C), BDOC removal was not significantly affected by water temperature (see Figure 6-2., p-value = 0.8), as was the case on 0-d PAC. Because BDOC removal is similar on 0-d or 60-d PAC, the increase in DOC removal with temperature on colonized PAC is attributed to the impact of temperature on RDOC adsorption. It can therefore be concluded that biodegradation is not the

primary mechanism responsible for DOC removal on colonized PAC in SW. For modeling purposes, the contribution of biodegradation to DOC removal on 10-d and 60-d PAC will therefore be neglected.

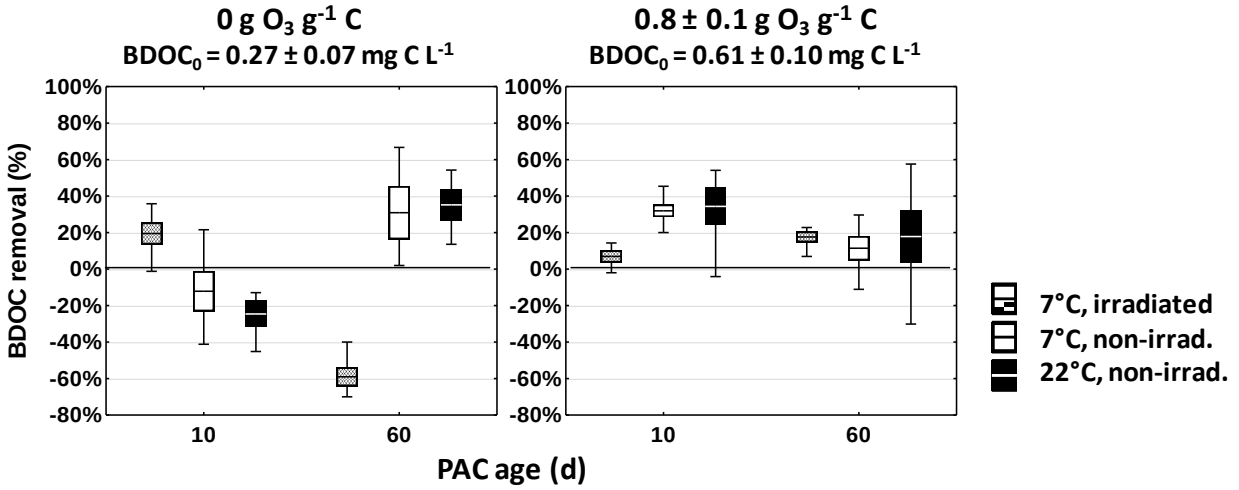

Figure 6-3 : Impact of gamma irradiation and temperature on BDOC removal in SW and pre-O_3 SW. 10-d and 60-d PAC were used at a concentration of 9.5 ± 0.8 g L^{-1}. The boxes represent the mean removal ± the standard error, and the whiskers correspond to the minimal and maximal removals.

6.3.4.2 Model development

Under the conditions investigated, adsorption was concluded to be the main mechanism for DOC removal in the PAC contactor of an HMP operated at high PAC ages and fed with an influent presenting a low BDOC concentration. However, the suspensions of aged PAC are composed of a distribution of ages. This is of paramount importance, as the adsorption capacity is influenced by both the preloaded NOM and the quantity of biomass on the PAC. The contribution of each of the aged fractions to the removal of DOC is thus expected to vary and should be accounted for. In this section, the DOC removal in the PAC contactor of an HMP operated at steady-state is modeled. The batch experiments provide data to estimate the kinetic parameters and adsorption capacity of the PAC used during the tests.

At first, the entire mass of PAC was considered to have the same age (θ, in d). This condition (often assumed in pilot studies) occurs when the PAC is aged in a contactor that is never purged.

Under this mode of operation, the DOC removal is expected to follow a breakthrough curve similar to what is observed in adsorption filters (Eq. 6-1).

$$P_t = P_\theta \times (1 - exp^{-K \times t}) \qquad \text{Eq. 6-1}$$

Where P_t is the percentage of DOC removed, K is a kinetic parameter (in min^{-1}), t is the HRT (in min) and P_θ is the theoretical maximal percentage of DOC that can be removed, a parameter that depends on both the DOC and PAC characteristics. P_θ corresponds to the residual maximal adsorption capacity of the PAC of a given age (in %).

Figure 6-1 demonstrates that DOC removal is not proportional to the PAC concentration. Given the low initial DOC concentration, there were more adsorption sites available than there was NOM to be adsorbed (Stoquart et al., 2013). The k-value was observed to be proportional to the amount of adsorption sites available and was thus proportional to the PAC concentration in the carbon contactor. Under these assumptions, Eq. 6-1 becomes Eq. 6-2:

$$P_t = P_\theta \times \left(1 - exp^{-k \times [PAC] \times t}\right) \qquad \text{Eq. 6-2}$$

Where k is a new kinetic parameter (in L g^{-1} min^{-1}) and $[PAC]$ is the PAC concentration in the carbon contactor of the HMP (in g dw L^{-1}).

During steady-state pilot-plant operation, the PAC is retained in the carbon contactor by low pressure membranes. The PAC age is managed by a system of frequent PAC purges/replenishments to maintain the targeted mean PAC age. The DOC removal was monitored twice in our HMP pilot plant during an aging period of 90 days (data not shown). In both cases, the PAC was not purged and the PAC age therefore increased with time. This approach revealed the relationship between P_θ (in %) and the age of PAC (θ) (see Eq. 6-3).

$$P_\theta = P_{MAX} \times \theta^{-b}; \quad \theta \geq 1\ d \qquad \text{Eq. 6-3}$$

Where P_{MAX} is the apparent maximal percentage of DOC removed by the PAC, which corresponds to the maximal performance of virgin PAC in the operating conditions tested (in %). This value is directly related to the adsorbable fraction of DOC in the NOM. The parameter b represents the impact of θ on the adsorption capacity of the PAC (in d^{-1}), i.e., the degree of exhaustion of the PAC.

As introduced earlier, the PAC gathered from a contactor operated at steady-state is normally composed of various fractions presenting different ages. The total percentage of DOC removed during the kinetics assays therefore corresponds to the sum of the percentages of DOC adsorbed by each of these fractions (see Eq. 6-4).

$$P = \sum_{i=0}^{\infty} f_i \times P_i \qquad \text{Eq. 6-4}$$

Where P is the DOC removal (in %), f_i is the fraction of PAC with an age of i days and P_i is the percentage of DOC adsorbed by a PAC presenting an age of i days. Including Eq. 6-2 and Eq. 6-3 in Eq. 6-4 gives Eq. 6-5, which is the final form of the model proposed herein.

$$P = \sum_{i=0}^{\infty} f_i \times P_{MAX} \times \theta^{-b} \times \left(1 - exp^{-k \times [PAC] \times t}\right) \qquad \text{Eq. 6-5}$$

The PAC age distributions of both 10-d and 60-d PACs were estimated using Excel (Microsoft Office 2007). Daily purges/renewals of PAC were begun once the PAC age had reached the target values of 10 d and 60 d. Calculations of the f_i-values were based on a daily renewal of 10% (10-d distribution) and 1.7% (60-d distribution) of the mass of PAC in the carbon contactor. The PAC age distribution was calculated assuming perfect mixing, which is not entirely representative of the real operation of the PAC contactor. The age distributions were considered stable after 50 days and 320 days of computed operation for the 10-d and 60-d distributions, respectively. This corresponds to approximately 5 times the mean age of the distribution. The PAC contactor was therefore operated at steady-state. A presentation of the theoretical distributions of the 10-d and 60-d PAC is provided as supplemental information (Figure A-3. 4).

DOC removals (P expressed in %) were modeled using Eq. 6-5. The dataset obtained for colonized PAC was divided into 7 groups, as modeling was realized based on results obtained in a single water matrix at one given temperature. Table 6-2 presents the parameters of the model (k, b, P_{MAX}) obtained by nonlinear regressions. As the structure of the model does not allow a PAC age of 0 days, PAC age distributions were computed just before the daily dosage of virgin PAC. PAC ages are assumed to vary between 1 and 61 days for 10-d PAC and between 1 and 401 days for 60-d PAC. PAC with higher ages accounted for fractions inferior to 0.5% and were therefore

considered negligible. R^2 values vary between 0.62 and 0.85. The lowest R^2 values were obtained in conditions where the DOC removal was below 20%. A figure showing predicted versus observed values is provided as supplemental information (Figure A-3. 5).

Table 6-2 : Values of the modeled parameters under the various operating conditions tested.

Temperature (°C)	**Water Type**	**Ozone Dose (g O_3 gC^{-1})**	**P_{MAX} (%)**	**k (L g^{-1} min^{-1})**	**b (d^{-1})**	**R^2**
22 ± 1	SW	0.0 ± 0.0	82%	0.96	0.36	0.85
		0.8 ± 0.0	80%	0.13	0.45	0.62
		1.5 ± 0.1	54%	0.10	0.26	0.71
7 ± 1	SW	0.0 ± 0.0	75%	0.29	0.56	0.72
		0.7 ± 0.0	29%	0.41	0.39	0.63
	RW	0.0 ± 0.0	57%	0.08	0.11	0.84
		0.7 ± 0.0	43%	0.06	0.16	0.84
	Mean-value		60%	0.29	0.33	-
	MAX		82%	0.96	0.56	-
	MIN		29%	0.06	0.11	-

6.3.4.3 Sensitivity analysis

The impact of *b*, *k* and P_{MAX} on DOC removal is illustrated in the sensitivity analysis presented in Figure 6-4, where the PAC concentration was set to 10 g L^{-1} and the HRT to 30 min. The baseline curve in Figure 6-4 was built based on the mean values of the parameters (Table 6-2). Min and max values refer to the parameter investigated, while baseline values were maintained constant for the two other parameters. The sensitivity analysis was conducted on each parameter in sequence. As supplemental information, Figure A-3. 6 provides simulations of DOC removal by aged PACs (1-d to 100-d) in various matrices and temperature conditions based on the parameter values in Table 6-2. The PAC contactor is assumed to be operated continuously (no PAC age distribution).

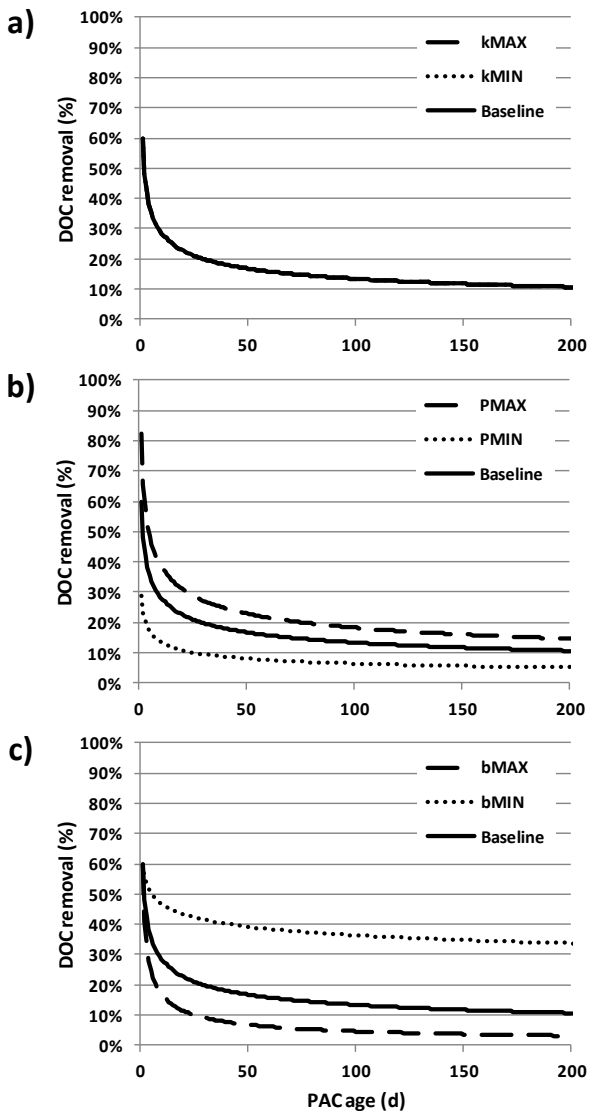

Figure 6-4 : Sensitivity analysis for *k, b* and P_{MAX} values. DOC removals (%) are predicted for a homogenously aged PAC. The PAC concentration is 10 g L^{-1} and the HRT is 30 minutes. The baseline curve is built using the mean value found for each parameter.

Variations in *k*-values did not appear significant (see Figure 6-4a). As the *k*-parameter describes the adsorption kinetics, a 30-min HRT is sufficient to reach pseudo-equilibrium in the contactor. In fact, k-values significantly impacted DOC removal for HRT values lower than 5 min. The results are coherent with data presented in the literature. For example, Treguer et al. (2010) did not notice any impact of matrix pre-ozonation on DOC adsorption kinetics. DOC diffusion is commonly considered non-limiting due to the thin boundary layer of PAC (Najm, 1996), which explains the non-significant impact of water temperature.

P_{MAX} is the maximal removal percentage reachable by the virgin PAC used under the conditions investigated. Variations in P_{MAX} values due to changes in the water temperature or water matrix were significant (Figure 6-4b). The capacity of the virgin PAC varies between 29% and 82% under the operating conditions tested. As expected, P_{MAX} increased with water temperature. Changing from i) a non-O_3 to pre-O_3 water matrix and ii) RW to SW led to lower P_{MAX} values (Table 6-2). As discussed earlier, pre-O_3 reduces the adsorbability of the DOC, resulting in a decrease of P_{MAX}. In contrast, the initial DOC concentration of RW is higher and richer in aromatic hydrophobic compounds (higher SUVA value). These molecules are preferentially adsorbed by PAC (Dabrowski et al., 2005). In addition, the PAC was aged in SW and pre-loaded with NOM from SW, while RW is composed of larger hydrophobic molecules that do not compete for the same adsorption sites. This partially explains the greater apparent capacity (P_{MAX}) obtained in RW than in SW for the same virgin PAC.

The *b*-parameter represents the exhaustion of the PAC. The higher the *b*-value is, the lower the adsorption capacity of the aged PAC. For example, the maximal DOC removal on 60-d PAC varied between 8% and 37% in the operating conditions tested (see Figure 6-4c). As expected, *b* decreased at higher temperature. This reflects the previously discussed improved efficiency of the PAC under these conditions. As for P_{MAX}, changes in the water matrix also increased the efficiency of the older PAC. The difference between the RW and the SW curves at 7°C in Figure A-3. 6 is therefore reflected by the b-values presented in Table 6-2. The lowest *b*-value was found in RW, which resulted in higher performance and therefore a greater usage of the residual adsorption capacity. As for P_{MAX}, the initial DOC concentration and the pre-exposure of PAC to a different water matrix (i.e., SW) explains the observed results.

6.3.4.4 Usage of a PAC age distribution

The main feature of the model developed herein is the integration of the PAC age distribution in DOC removal modeling in an HMP. Figure 6-5 illustrates the respective contribution to DOC removal of the various fractions of PAC that constitute the 10-d and 60-d PAC age distributions. The efficiencies in SW and RW are compared under the same operating conditions (7°C, HRT=30 min, PAC concentration = 10 g L^{-1}).

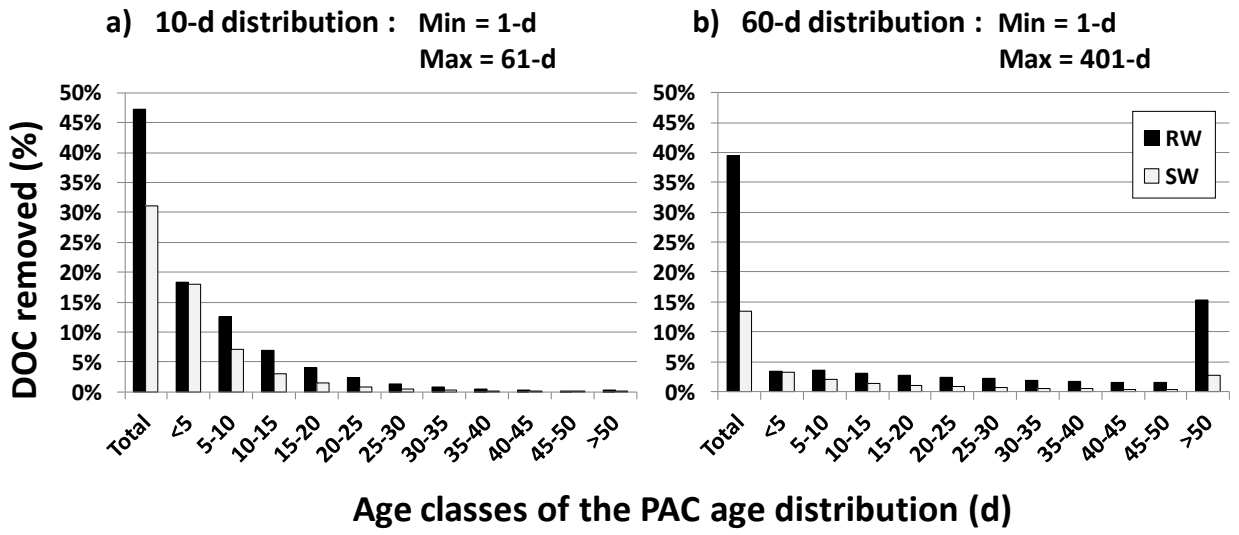

Figure 6-5 : Contribution of the age classes constituting the 10-d and 60-d PAC to DOC removal in SW and RW at 7°C. The HRT is set to 30 min and the PAC concentration to 10 g L^{-1}.

At 7°C in SW, 80% of the removal was reached by the fraction of PAC with an age of 10 d and less (10-d PAC age distribution) or 25 d and less (60-d PAC age distribution). These fractions corresponded respectively to 65% and 34% of the available PAC (i.e., 6.5 and 3.4 g L^{-1} out of the 10 g L^{-1} available). Figure 6-5 indicates that the majority of DOC removal happens on the younger fraction of PAC. When changing the water matrix from SW to RW, it is worth noting that the older fraction also contributed. As a result, 80% of the total removal was achieved by PAC aged 15 d and less for the 10-d distribution (79% of the PAC available) and 50 d and less for the 60-d distribution (57% of the PAC available). The older fraction of the PAC distributions still presents a significant residual adsorption capacity, which could be useful in the case of changing influent water quality or for other objectives such as micropollutant control.

6.4 Discussion

6.4.1 Modeling DOC removal in the HMP

The aged PAC used in the present study was colonized in SW with a low BDOC concentration. The existence of biodegradation activity is not questioned, as the quantity of active biomass measured (per g of activated carbon) was similar to that observed for biological filters (Stoquart et al., 2014a). However, the importance of this biodegradation activity on total DOC removal was demonstrated to be marginal compared to DOC adsorption. DOC removal on aged PAC was

therefore modeled as an adsorption process only. The BDOC release observed on 0-d PAC was not considered. Indeed, the amount of BDOC released per liter of water treated remains well below the DOC detection limit when operating the HMP under the range of operating conditions tested. Considering the observed BDOC release of 0.04 mg C g^{-1}, a minimal concentration of 2 g L^{-1} of virgin PAC would be required to release a detectable amount of BDOC.

The proposed model is valuable for understanding the residual adsorption capacity of aged PAC in an HMP operated at steady state. In particular, the performed assays demonstrated that PAC with age distributions reaching as high as 400 d still presented some residual adsorption capacity. However, the developed model demonstrated that this fraction contributed marginally compared to the younger fraction of PAC, which was responsible for most of the treatment's performance. To predict DOC removal in other matrices or temperatures, additional datasets would be required to define the values of the three parameters of the model. As a negative impact of high PAC ages has previously been reported (Léveillé et al., 2013), PAC age distributions centered on higher values (e.g., >100 d) would also require further testing.

One of the limitations of the present model is the exclusion of biodegradation. It is likely that in other colonizing conditions, the relative importance of biodegradation and adsorption to DOC removal will vary. As an example, BDOC removals tended to increase with PAC age in RW at 7°C, which suggests active biodegradation, an effect that is expected to be reinforced at 22°C. Therefore, in other cases, adding a biodegradation term could be essential. However, for applications of the model in low BDOC waters such as unozonated settled waters, neglecting biodegradation is recommended.

Another limitation of the current model is the fact that temperature is not directly incorporated. Studying DOC adsorption on a wider range of temperatures would be required to integrate the temperature effect in the model. This task was unsuccessfully attempted with the current dataset, but the availability of only two temperatures (7 and 22°C) limited the modeling possibilities.

6.4.2 Recommendations for the optimization of PAC reactor operating conditions

The PAC age was demonstrated to be the primary operating parameter that should be optimized to reach the targeted DOC removals. A major loss in removal efficiency was observed when switching from virgin PAC to 10-d PAC and subsequently to 60-d PAC. Similar losses of efficiency have been reported in the literature. Seo et al. (2004) reported decreases in DOC

removal from 80 to 30% within 90 days of operation. Within 10 d of operation, Williams et al. (2007) noticed the same range of losses. The modeling of DOC removal in an HMP operated at steady state demonstrates that the younger fraction of PAC is responsible for most of the treatment. Most of time, the adsorption capacity of the older fraction of PAC is not utilized. However, a residual adsorption capacity was indicated in the older fraction, which could be useful in case of a drastic change of the influent characteristics.

The PAC concentration was demonstrated to be an operating parameter of minor significance when it was maintained between 1 and 10 g L^{-1}, in particular when its influence was compared to that of the PAC age in SW. However, DOC removal increases with higher concentrations were noticed in RW. Kim et al. (2007) observed a 42% increase in DOC removal when raising the PAC concentration from 4 g L^{-1} to 40 g L^{-1} under low PAC ages (0-5 days). However, this represents a major change in operating conditions. Markarian et al. (2010) also noticed an increased efficiency when the PAC concentration was raised from 5 to 25 g L^{-1} under a low PAC residence time. In general, the effect of increasing the PAC concentration depends on the nature and quantity of NOM to be removed. In the present study, the lower importance of the PAC concentration is attributed to the fact that in most cases, the availability of adsorption sites was not the limiting factor for DOC removal. However, the PAC concentration has been demonstrated to impact the fouling of low-pressure membranes (Stoquart et al., 2012). Its optimization remains therefore important, especially in conditions where the adsorption capacity is a limiting factor. Proper PAC selection is also an important parameter for the maximization of process performance. During this project, we selected a wood-based PAC favorable for biological activity, as we were expecting biodegradation to be an important mode of action of aged PAC. Considering the importance of adsorption under the investigated conditions, PAC selection should be based on maximizing adsorption performance rather than biodegradation.

The contact time was not found to be a key operating parameter in the operating conditions tested; the efficiency of the process was mainly due to adsorption. The results of the kinetics study demonstrated that most of the adsorption occurred almost immediately. However, the relative importance of the contact time will vary with the HMP influent. Indeed, in the case of a higher BDOC content, biodegradation could play a significant role in DOC removal (cf. biological filters). In HMP operated with post-O_3 filtered water and a 30-d PAC, Markarian et al. (2010) observed an improvement in BDOC and ammonia removal when increasing the HRT

from 15 to 30 minutes. No further improvement was noticed after 30 minutes. Therefore, when the biological activity is significant for the performance of the process (e.g., ammonia removal), HRT should be optimized, as the biodegradation kinetics will affect the speed of DOC removal. For applications targeting mostly adsorption, the use of shorter contact times (e.g., 15 min) should be considered to reduce capital costs.

6.5 Conclusions

The following conclusions are drawn from this study:

- Biodegradable DOC release in water samples was observed when applying high concentrations of virgin PAC (i.e., 10 g L^{-1}). In settled waters, the net release was estimated to be 0.04 ± 0.02 mg C g^{-1} PAC.
- On PAC aged in settled waters, the residual adsorption capacity was shown to be the mechanism responsible for DOC removal. Biodegradation activity could be considered marginal in these conditions.
- DOC adsorption was favored at higher temperature. At 22°C, DOC removal in SW was approximately 80%, 44% and 25% with 0-d, 10-d and 60-d PAC, respectively.
- The model developed indicates that 80% of DOC removal at 7°C is reached by the fraction of PAC aged 10 d and less (for a 10-d average PAC) or 25 d and less (for a 60-d average PAC).
- Under non-limiting adsorption site availability, the PAC age was the key operating parameter for optimization. Therefore, the PAC concentration was of lower importance in the range of conditions tested.
- As adsorption was the main mechanism, the hydraulic retention time was not a key operating parameter.

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CHAPTER 7 ARTICLE 6 – MICROPOLLUTANT REMOVAL IN THE AGED POWDERED ACTIVATED CARBON CONTACTOR OF A HYBRID MEMBRANE PROCESS

This chapter presents the last publication of this research project. It is devoted to the demonstration of the potential of HMPs using aged PAC to remove a mixture of micropollutants. HMPs are most of time operated with virgin PAC for the removal of micropollutants. However, only one study reported the potential of aged PAC to adsorb atrazine. In this chapter, a mixture of micropollutants of varied characteristics was spiked in settled water. Micropollutants removal kinetics were monitored in presence of virgin and aged PAC. 95% of all the micropollutants were adsorbed in less than 5 minutes on all PACs tested. This chapter is a paper submitted to *Journal of Hazardous Materials*.

MICROPOLLUTANT REMOVAL IN THE AGED POWDERED ACTIVATED CARBON CONTACTOR OF A HYBRID MEMBRANE PROCESS

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ABSTRACT

The main objective of this study is to present a first demonstration of the potential of the powdered activated carbon (PAC) contactor of a hybrid membrane process using aged PAC to remove a mixture of micropollutants spiked at environmentally-relevant concentrations. Three PACs of varying ages (1 g/L of 0-d, 10-d and 60-d) were added in settled water (SW) and pre-ozonated SW. Under these operating conditions, direct competition with natural organic matter was not evidenced when substituting the SW water matrix with the pre-O3 SW matrix. All the micropollutants were rapidly adsorbed on the three PACs, and removals superior to 95% were reached within 5 min for all the micropollutants investigated. PAC aging decreased the adsorption kinetics of ATZ, DEA and CAF, but had no impact on the adsorption capacity for these contaminants. At low hydraulic retention time (< 15 min), PAC age is thus expected to impact significantly the process performance. To conclude, this study demonstrates that an HMP operated under typical conditions needed to achieve the removal of ammonia and DOC, has the potential to efficiently remove a wide variety of micropollutants and comply with current WHO regulations for MC (1 µg/L) and ATZ (2 µg/L).

KEYWORDS

Micropollutants - Hybrid Membrane Process - Aged PAC - Drinking water - Adsorption kinetics

7.1 Introduction

Micropollutants (MPs) are defined as any compound from natural and anthropogenic sources found at µg/L concentrations or lower in natural surface waters. They include algal toxins, pesticides, pharmaceutical residues, hormones, flame-retardants, plasticizers, perfluorinated compounds, and many other classes of compounds. They are brought to aquatic ecosystems through runoff or the release of waste waters as most of these substances are not well removed by wastewater treatment (Miège et al., 2009). These MPs have been detected in water sources used for water potabilization and at trace concentrations in drinking water (Coupe et al., 2004; Huerta-Fontela et al., 2011). Even if most of them are currently unregulated, they represent a growing concern for the water industry. Their impact on public health is often unknown, especially when

considering the toxicity of mixtures of a large diversity of chemical compounds, which can potentially have synergic deleterious effects.

The potential for many MPs to escape conventional drinking water treatment was demonstrated (Stackelberg et al., 2004). Pharmaceuticals have been detected after coagulation (Stackelberg et al., 2007; Ternes et al., 2002), slow sand filtration (Ternes et al., 2002) and chlorination (Stackelberg et al., 2007). More advanced technologies are therefore needed to provide an effective barrier against MPs (Ternes et al., 2002). Activated carbon adsorption is amongst the best technologies for advanced drinking water treatment. Hybrid membrane processes (HMPs) couple the usage of powdered activated carbon (PAC) with low pressure membrane filtration. The PAC contactor targets the removal of dissolved contaminants while the membrane filtration ensures the efficient elimination of particles and pathogenic parasites (Stoquart et al., 2012).

In most published work evaluating the performance of the HMP to remove MPs, PAC residence times are mostly maintained below 1 d and reaching 7 d (Stoquart et al., 2012). The operation of the HMP with high PAC residence times (aged PAC) is currently under investigation as it reduces the operating costs whilst providing the benefit of adding to adsorption, a biological removal component, thanks to the PAC microbial activity (biodegradation of the biodegradable fraction of DOC (BDOC) and nitrification). However, the adsorption performance in HMPs using aged PAC may decrease due to the partial or full exhaustion of the adsorption sites. Recent publications from our group demonstrated that the residual adsorption capacity of 10-d and 60-d PAC contributed significantly to ammonia (Stoquart et al., 2014b) and NOM removal (Stoquart et al., Submitted). It is therefore of interest to evaluate if these conclusions could also extend to the case of MPs.

Studies using older activated carbon (often simulated by NOM preloading at lab-scale) demonstrated that NOM pre-loading decreased the surface area available for trichloroethylene adsorption and evidenced an increased competition between NOM and trichloroethylene for adsorption sites (Kilduff et al., 1999). Adsorption capacity decreased due to direct competition with NOM or to NOM adsorbing to PAC and blocking the access to micropores (pore blockage or restriction) (Li et al., 2003a; Matsui et al., 2003; McDonough et al., 2008). To a lesser extent, NOM-preloading of PAC also slows down adsorption kinetics, due to pore blockage (Matsui et al., 2003). The relative importance of direct competition and pore blockage by NOM depends on

the nature of the NOM along with the surface characteristics of the PAC (Pelekani et al., 2000). On the other hand, PAC aging in the HMP leads to its colonization by heterotrophic and nitrifying bacteria (Stoquart et al., 2014a; Stoquart et al., 2014b), a phenomenon not taken into account by these studies. Activated carbon coated by a biofilm was shown to have reduced adsorption capacity for perchlorinated biphenyls(McDonough et al., 2008) and toluene (Zhao et al., 1999). To the best of our knowledge, the only published work about the impact of PAC aging on MPs removal in HMPs was performed for atrazine (ATZ) and concluded that ATZ adsorption capacity and kinetics were decreased by PAC aging (Lebeau et al., 1998; Lebeau et al., 1999).

The main objective of this study is to present a first demonstration of the potential of using an HMP with aged PAC to remove a mixture of micropollutants spiked at environmentally-relevant concentrations. Three PACs of varying ages (0-d, 10-d and 60-d) were added in two water matrices. As HMPs are operated in continuous flow with a constant PAC dosage, adsorption equilibrium is not reached in the contactor and emphasis was put on kinetics. Assays using abiotic PAC were also carried out to discriminate the role of adsorption from that of biodegradation on the removal of the micropollutants.

7.2 Experimental

7.2.1 Powdered activated carbon

A wood-based PAC (Picahydro LP 39) was used (median diameter 24.2 µm). PAC aging was carried out in an industrial HMP pilot facility described by Léveillé et al. (2013). The pilot-plant consisted of two parallel treatment chains in which ultrafiltration membranes were immersed in a PAC suspension. Both contactors were operated at steady-state thanks to a daily purge of a fraction of the PAC and its replacement with virgin PAC. In the two parallel treatment trains, mean PAC ages were set to 10-d and 60-d with the following targeted operating concentrations: 4 g L^{-1} (3.5±1.2 g L^{-1}) for the 10-d and 10 g L^{-1} (9.8±1.1 g L^{-1}) for the 60-d. The selected PAC ages allowed PAC colonization by heterotrophic and autotrophic nitrifying bacteria (Stoquart et al., 2014a; Stoquart et al., 2014b). Both HMP contactors were operated with a hydraulic retention time (HRT) of 67 min. PAC contactors were fed with alum-settled water from the Ste-Rose drinking water treatment plant (Laval, Qc, Canada) (pH = 6.70±0.11; turbidity = 0.62±0.40 NTU; UV_{254} = 0.056±0.007 cm^{-1}; DOC = 3.02±0.30 mg C L^{-1}; BDOC=0.27±0.11 mg C L^{-1}, alkalinity =

20±2 mg $CaCO_3$ L^{-1}, between winter 2011 and summer 2012). An abiotic control for colonized 60-d PAC was produced by gamma-irradiation in Nordion Inc. facilities (Laval, Qc, Canada). Irradiation dosage (12.5 kGy) was optimized to inhibit the activity of the fixed bacterial biomass without affecting the adsorption characteristics of the colonized PAC, as recommended by Stoquart et al. (2013).

7.2.2 Micropollutants mixture

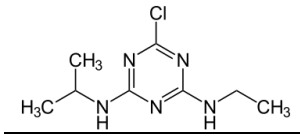
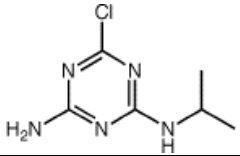
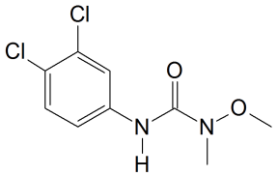
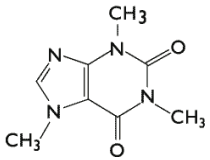
Assays were conducted using a mixture of micropollutants including hormones, pesticides, pharmaceutical and personal care products and one cyanotoxin. Table 7-1 summarizes the characteristics, the initial concentrations at which each micropollutant was spiked, and the analytical method detection limit (MDL). MPs were selected to provide a wide range of usage and chemical properties. They were spiked as a mixture at environmentally-relevant concentrations into settled water (SW) or into the same SW pre-ozonated beforehand (pre-O_3 SW; 0.85 g O_3 g^{-1}C). Characteristics of both water matrices are presented in Table 7-2.

All standards (purity ≥ 97 %), namely atrazine (ATZ), deethylatrazine (DEA), linuron (LIN), caffeine (CAF), sulfamethoxazole (SMX), carbamazepine (CBZ), diclofenac (DCF), progesterone (PROG) and medroxyprogesterone (MEDRO) were purchased from Sigma-Aldrich Canada (St. Louis, MO). The isotopically-labeled internal standards [13C3]-atrazine, carbamazepine-[d10], [13C3]-caffeine, and [13C6]-sulfamethoxazole were obtained from Cambridge Isotope Laboratories, Inc. (Andover, Massachusetts, USA), whereas diclofenac-[d4] was obtained from C/D/N Isotopes (Pointe-Claire, Qc, Canada). Individual stock solutions were prepared in methanol at a concentration of 1000 mg/L and kept at -20ºC for a maximum of six months. Two primary mix working solutions were prepared. The first mix consisted of ATZ, DEA and LIN at a concentration of 80 mg/L by dilution of individual stock solutions aliquots in HPLC grade water. The second mix consisted of CAF (concentration of 8 mg/L), SMX, CBZ, DCF, PROG and MEDRO at (concentration of 800 µg/L), by dilution of individual stock solutions aliquots in HPLC grade water. These mixes were spiked in the water matrices to reach the targeted initial concentrations. All organic solvents and water used for dilutions were of HPLC grade purity from Fisher Scientific (Whitby, On, Canada).

Microcystin (MC) was extracted from a toxic strain of *Microcystis aeruginosa* grown on artificial seawater medium (Gorham et al., 1964). The strain was cultured at 26 ± 1°C and under a 12:12-h

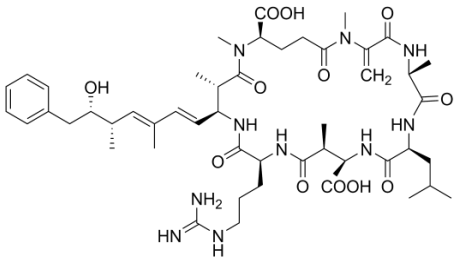
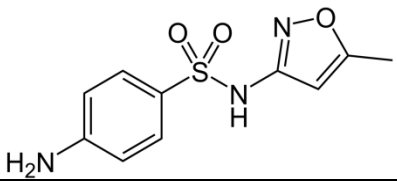
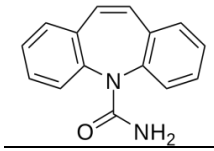
light:dark cycle. Sufficient aeration and a light intensity of 70 μmol/(s m) were provided during the culture. Cells in stationary phase were harvested through glass fiber filters. These were frozen-thawed twice and then extracted for 15 min in a bath ultrasonicator with 2 mL of 75% methanol, following the procedure of Meriluoto et al. (2005). The extracts were recovered after centrifugation at 10 000*g* for 10 min, filtered through a C_{18} cartridge, evaporated to dryness under nitrogen and kept at -80°C until further analysis. The frozen samples were reconstituted by suspension in 75% methanol.

Table 7-1 : Micropollutants characteristics, initial spiked concentrations and method detection limits

Micropollutant	Usage	MW[a] (g/mol)	$LogD_{ow}$[b] (pH 6.5)	pKa	FOSA[c] (Å/molecule)	$^{8}X_{p}$[d] (-)	Initial concentration (µg/L)	MDL (ng/L)
Atrazine (AZ) 	Herbicide	215.1	2.6	1.7 [+/0]	314.7	0.511	16.8 ± 1.6	1
Deethylatrazine (DEA) 	Atrazine metabolite	187.6	1.5	1.4 [+/0]	NA	NA	17.4 ± 1.7	1
Linuron (LIN) 	Herbicide	249.1	3.0	12.1 [+/0]	NA	NA	15.9 ± 1.0	3
Caffeine (CAF) 	Stimulant	194.2	-4.0	10.4 [+/0]	239.0	0.506	2.2 ± 0.1	7

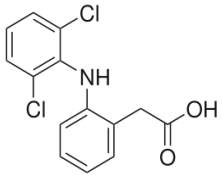
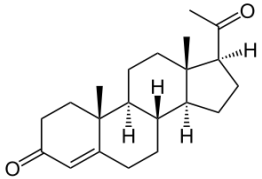
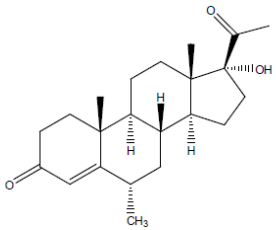
[+/0] transition from cationic to neutral form; [a]MW=molecular weight; [b]$D_{OW} = \frac{K_{OW}}{1+10^{pH-pK_a}}$ for an acid and $D_{OW} = \frac{K_{OW}}{1+10^{pK_a-pH}}$ for a base, pKa and $LogK_{ow}$ values from (Pavlovic et al., 2013; Westerhoff, Yoon, et al., 2005; Xu et al., 1999), [c]FOSA=molecule hydrophobic surface area; [d] $^{8}\chi_{p}$ = number of unique 8-bond path, values from (Redding et al., 2009).

Table 7-1: Micropollutants characteristics, initial spiked concentrations and method detection limits (continue)

Micropollutant	Usage	MW[a] (g/mol)	$LogD_{ow}$[b] (pH 6.5)	pKa	**FOSA[c] (**Å/molecule)	$^{8}X_{p}$[d] (-)	Initial concentration (µg/L)	MDL (ng/L)
Microcystin (MC)  (MC-LR)	Cyanotoxin	909-1115	-1.26 (MC-LR)	pK1 2.09 pK2 2.19 pK3 2.48 [-]	992	3.62	33.5 ± 16.2	100
Sulfamethoxazole (SMX) 	Antibiotic	253.3	0.8	pK1 1.7 pK2 5.8 [-]	96.4	0.492	0.16 ± 0.02	3.5
Carbamazepine (CBZ) 	Anti-convulsant + mood stabilizing	236.3	2.4	pK1 2.3 pK2 13.9 [0]	43.2	1.748	0.19 ± 0.01	0.5

[0] neutral molecule, [-] net negative charge at pH 6.5; [a]MW=molecular weight; [b]$D_{OW} = \frac{K_{OW}}{1+10^{pH-pK_a}}$ for an acid and $D_{OW} = \frac{K_{OW}}{1+10^{pK_a-pH}}$ for a base, pKa and $LogK_{ow}$ values from (de Maagd et al., 1999; Fick et al., 2010; Westerhoff, Yoon, et al., 2005); [c]FOSA=molecule hydrophobic surface area; [d] $^{8}\chi_{p}$ = number of unique 8-bond path, values from (Redding et al., 2009)

Table 7-1: Micropollutants characteristics, initial spiked concentrations and method detection limits (continue)

Micropollutant	Usage	MW[a] (g/mol)	$LogD_{ow}$[b] (pH 6.5)	pKa	**FOSA[c] (**Å/molecule)	$^{8}X_{p}$[d] (-)	Initial concentration (µg/L)	MDL (ng/L)
Diclofenac (DCF) 	Anti-inflammatory	296.2	4.6	4.2 [0/-]	24.4	1.066	0.15 ± 0.01	3
Progesterone (PROG) 	Steroid	314.2	3.9	- [0]	430	3.085	0.13 ± 0.02	20
Medroxyprogesterone (MEDRO) 	Synthetic steroid	344.5	2.7	- [0]	NA	NA	0.15 ± 0.02	6

[0/-] transition from anionic to neutral form. [0] neutral molecule; [a]MW=molecular weight; [b]$D_{OW} = \frac{K_{OW}}{1+10^{pH-pK_a}}$ for an acid and $D_{OW} = \frac{K_{OW}}{1+10^{pK_a-pH}}$ for a base, pKa and $LogK_{ow}$ values from (Fick et al., 2010; Westerhoff, Yoon, et al., 2005); [c]FOSA=molecule hydrophobic surface area; [d] $^{8}\chi_{p}$ = number of unique 8-bond path, values from (Redding et al., 2009)

Table 7-2 : Characteristics of the water matrices used

Parameter	Settled water (SW)	Pre-ozonated settled water (pre-O_3 SW)	Units
pH	6.52	6.49	-
Turbidity	0.314	0.243	NTU
DOC	2.62	2.32	mg C/L
UV_{254}	0.0484	0.0210	cm^{-1}
Alkalinity	42	64	mg $CaCO_3$/L
Temperature	22	22	°C

7.2.3 Micropollutants removal kinetics

The micropollutants removal kinetics were performed at lab-scale on virgin (0-d), 10-d, 60-d and 60-d gamma-irradiated PAC at a concentration of 1.1±0.1 g/L. The 0-d PAC was neutralized (pH = 7) with a 1M NaOH solution 12-24 hours before the assays. PAC suspensions (virgin or colonized) were filtered on a 20 µm paper filter (Grade 41, Whatman®) to recover a dense PAC cake. Dry weights of the cake were evaluated in triplicate with the 2540-B technique (American Public Health Association (APHA) et al., 2012). Portions of the PAC cake were resuspended in 2-L samples of the water matrices presented above (SW and pre-O_3 SW; Table 7-2). Experiments were conducted at 22°C at lab scale using colonized PACs (10-d and 60-d) acclimated to that same temperature at the pilot-plant.

Removal of micropollutants was monitored by collecting two samples of 10 mL from the 2-L PAC suspension at increasing contact times (1, 5, 10, 15, 45 min, 2 h, 6h). 24h and 48h contact time samples were also taken during the monitoring of 10-d and 60-d PAC kinetics. The samples were immediately filtered on a 0.2 µm PVDF GD/X syringe filter (Whatman®) to ensure the immediate separation of the PAC from the water.

7.2.4 Analytical methods

Except for microcystins, the selected compounds were analyzed by automated solid phase extraction coupled to liquid chromatography tandem mass spectrometry (online SPE-LC-MS/MS). The methodology is described in detail in Fayad et al. (2013) for the analysis of hormones while for the other compounds, the method was modified from Garcia-Ac et al. (2009).

Briefly, the pre-concentration was performed using the Equan^{TM} (Thermo Fisher Scientific, Waltham, MA) system. The online SPE was achieved using a Hypersil Gold aQ (20 mm x 2 mm, 12 µm particle size) column and chromatographic separation was done with a Hypersil Gold (100 mm x 2.1mm, 1.9 µm particle size) column kept at 55^{o}C. A binary gradient made of (A) HPLC grade water with 0.1% formic acid, and (B) methanol with 0.1% formic acid was used to achieve chromatographic separation in 7 min. The ionization of the selected compounds was achieved using an atmospheric pressure chemical ionization source (APCI) in positive mode (PI). The ionization of selected compounds was achieved using the Ion Max API Source mounted on a Quantum Ultra AM triple quadrupole mass spectrometer by Thermo Fisher Scientific (Waltham, MA) operated in selected reaction monitoring (SRM) mode for quantification and detection.

Microcystin (MC) analyses were conducted in duplicates using an Abraxis Microcystin ADDA ELISA Plate (an enzyme linked immunosorbent assay - Abraxis LLC, Pennsylvania, USA) which provide results expressed as equivalent MC-LR concentrations. The MDL and coefficient of variation of the method are 0.1 µg/L and <15%, respectively (as given by the manufacturer).

7.3 Results

7.3.1 General observations

The initial MPs' concentrations measured in the water matrices after spiking corresponded to the targeted initial concentrations. MPs' initial concentrations in the water matrices utilized were thus negligible compared to the spiked concentrations. Figure 7-1 illustrates the type of profiles obtained during the monitoring of micropollutants removal by aged PAC (60-d). The MDL value was attributed to samples below MDL. The kinetics' profiles are only presented for ATZ, CAF, MC, CBZ, and PROG removals by 60-d PAC in SW (Figure 7-1a) and in pre-O_3 SW (Figure 7-1b). The kinetics' profiles for PROG and MEDRO were similar with both hormones' concentrations below MDL except at time 0 of the kinetics.

The contact time had a significant impact on the removal of most contaminants. Removals ranging from 54% (SMX on 60-d PAC in SW) to 99% (LIN on 10-d PC in SW) were reached within less than 1 minute. The concentration of most micropollutants decreased below MDL within the following 5 to 120 minutes depending on the PAC age. ATZ and DEA were the only compounds with detectable concentrations over the entire period of testing (7 h for 0-d PAC; 48 h

for 10-d and 60-d PACs). CAF was also detected after 48h on 60-d PAC only. Concentrations of ATZ, DEA and CAF decreased over time and adsorption equilibrium was reached after 6 hours on 10-d (ATZ, DEA) and 60-d PAC (ATZ, DEA, CAF). The other micropollutants were below MDL after 120 min.

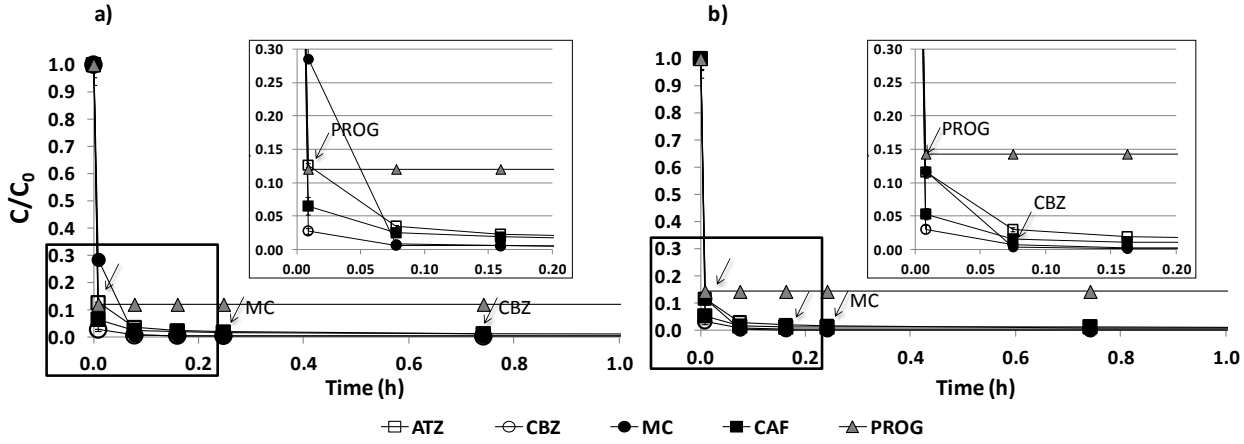


Figure 7-1 : Removal kinetics of ATZ (⊟), CAF (■), MC (●), CBZ (⊖) and PROG (▲) on 60-d PAC in a) SW and b) pre-O_3 SW. Arrows indicate the time after which data are below MDL.

7.3.2 MP removal on virgin PAC

Table 7-3 summarizes the contact time required to remove 1 Log (t_{90}) or 2 Log (t_{99}) of each MP in both water matrices (SW and pre-O_3 SW). These values were estimated based on interpolations between the two adequate sampling points. The MDL was attributed as a value to the samples in which the MP was not detected. For MPs with a MDL that did not allow measuring a 2 Log removal (SMX, DCF, PROG and MEDRO), the reported contact times in Table 7-3 correspond to the first sampling contact time when the micropollutant was not detected.

Table 7-3 : Contact time required to remove 1Log and 2Log and adsorption capacity (q_e) of micropollutants on virgin and colonized PAC in two water matrices

Micropollutants	PAC age (d)	t_{90} (min)			t_{99} (min)			q_e[(a)] (µg/g)	
		SW	pre-O_3 SW	R[(b)]	SW	pre-O_3 SW	R[(b)]	SW	pre-O_3 SW
Atrazine (ATZ)	0	0.4	0.4	1.0	5.7	9.3	1.6	14	14
	10	0.5	0.4	0.8	8.2	4.7	0.6	15	18
	60	1.3	0.9	0.7	81.9	44.5	0.5	14	15
	60 irrad.	0.5	0.5	1.0	44.4	33.6	0.8	17	17
Deethylatrazine (DEA)	0	0.4	0.4	1.0	4.4	4.3	1.0	15	14
	10	0.6	0.5	0.8	356.3	44.4	0.1	14	17
	60	2.7	2.5	0.9	>48h	>48h	-	15	15
	60 irrad.	0.6	1.3	2.1	>48h	>48h	-	19	17
Linuron (LIN)	0	0.3	0.4	1.3	4.4	9.3	2.1	>13	>12
	10	0.3	0.3	1.0	1.4	0.6	0.4	>15	>15
	60	0.3	0.3	1.0	2.2	2.3	1.0	>17	>14
	60 irrad.	0.3	0.3	1.0	1.8	1.7	0.9	>16	>15
Caffeine (CAF)	0	0.4	0.4	1.0	2.8	2.1	0.8	>2	>2
	10	0.4	0.3	0.8	78.7	2.3	0.03	>2	>2
	60	0.5	0.4	0.8	54.4	60.0	1.1	2.3	2
	60 irrad.	0.5	0.4	0.8	2.8	5.5	2.0	>2	>2
Microcystin (MC)	0	0.3	0.4	1.3	4.4	11.7	2.7	>25	>19
	10	0.5	0.6	1.2	3.2	4.0	1.3	>27	>23
	60	1.7	0.7	0.4	4.4	3.5	0.8	>27	>70
	60 irrad.	1.2	1.6	1.3	6.3	6.7	1.1	>29	>29
Sulfamethoxazole[(d)] (SMX)	0	0.3	0.3	1.0	>0.5	>0.6	1.2	>0.1	>0.1
	10	0.3	2.0	6.7	>0.6	>4.7	7.8	>0.2	>0.2
	60	2.5	6.7	2.7	>4.7	>9.8	2.1	>0.2	>0.2
	60 irrad.	2.7	2.4	0.9	>4.2	>4.2	1.0	>0.1	>0.1
Carbamazepine (CBZ)	0	0.3	0.4	1.3	17.4	9.3	0.5	>0.2	>0.2
	10	0.3	0.3	1.0	1.8	1.9	1.1	>0.2	>0.2
	60	0.3	0.3	1.0	3.5	3.7	1.1	>0.2	>0.2
	60 irrad.	0.4	0.3	0.8	1.8	3.3	1.8	>0.2	>0.2
Diclofenac[(d)] (DCF)	0	0.3	1.3	4.3	>4.4	>4.3	1.0	>0.1	>0.1
	10	1.6	0.4	0.3	>4.5	>4.7	1.0	>0.1	>0.1
	60	2.0	2.0	1.0	>4.7	>4.5	1.0	>0.1	>0.1
	60 irrad.	1.5	1.3	0.9	>4.2	>4.2	1.0	>0.1	>0.1
Progesterone[(c)] (PROG)	0	>0.5	>0.6	1.2	>0.5	>0.6	1.2	>0.1	>0.1
	10	>0.6	>0.6	1.0	>0.6	>0.6	1.0	>0.1	>0.1
	60	>0.5	>0.5	1.0	>0.5	>0.5	1.0	>0.1	>0.1
	60 irrad.	>0.6	>0.5	0.8	>0.6	>0.5	0.8	>0.1	>0.1
Medroxy-progesterone[(d)] (MEDRO)	0	0.3	0.4	1.3	>0.5	>0.6	1.2	>0.1	>0.1
	10	0.4	0.4	1.0	>0.6	>0.6	1.0	>0.2	>0.1
	60	0.4	0.4	1.0	>0.5	>0.5	1.0	>0.1	>0.1
	60 irrad.	0.5	0.4	0.8	>0.6	>0.5	0.8	>0.1	>0.1

[(a)] q_e was evaluated after a contact time of 6 hour: $q_e=([MP]_{0h}-[MP]_{6h})/[PAC]$

[(b)] $R= t_{pre\text{-}O3\ SW} / t_{SW}$

The reported t_{90} and t_{99} correspond to the contact time required to go below MDL. For the MPs for which the targeted [(c)]1Log or [(d)]2Log removal was not detectable.

As expected, the virgin PAC offered the highest MP removal efficiency under the investigated conditions. On 0-d PAC, t_{90} values were always inferior to 1 min for all the MPs in SW. Except for ATZ and CBZ, 0-d PAC provided t_{99} values (or decreased SMX, DCF, PROG and MEDRO concentrations below their respective MDL) within 5 min for all contaminants spiked in SW. Therefore, these results demonstrate that direct competition with the NOM in the water matrix

was overcome by the high amount of PAC available. When operating the HMP under adsorption mode only (0-d PAC), the PAC concentration tends to be largely inferior to 1 g/L for budgetary reasons. At lab-scale, Saravia et al. (2008) observed CBZ and DCF removals superior to 95% after 22 h in presence of 2.4 mg/L of DOC with a PAC concentration of 22 mg/L. In groundwater (2.1 mg DOC/L), 75% ATZ removal was achieved while using 576 mg PAC/L after 120 minutes with an initial concentration of 2 µg ATZ/L (Campos et al., 1998). Therefore, a lower efficiency than that observed in this study is expected when operating the HMP with virgin PAC due to the need to use lower concentrations. When operating the HMP with aged PAC, high PAC concentrations are recommended and concentrations ranging from 1 to 40 g/L have been reported (Stoquart et al., 2012).

7.3.3 Impact of irradiation on MPs removal

The removal kinetics were monitored on 60-d PAC and on irradiated 60-d PAC (abiotic control). For all the MPs investigated, a paired t-test revealed no statistically significant difference ($p = 0.20$). Therefore, even though colonized by bacterial biomass (Stoquart et al., 2014a), the 60-d PAC did not exhibit any MPs biodegradation. Half of the MPs tested (ATZ, DEA, LIN, SMX, CBZ) are not biodegradable. PROG was demonstrated as biodegradable in surface waters (Vanderford et al., 2003). Due to structural similarities with PROG, MEDRO is also expected to be biodegradable. CAF, MC, DCF biodegradation was observed in acclimated biological sand and GAC filters (Reungoat et al., 2011; Snyder et al., 2007; Wang et al., 2007; Zearley et al., 2012). Nonetheless, acclimation periods of 4 days (Ho et al., 2006) up to several months (Wang et al., 2007) have been reported before the onset of MC biodegradation in biological filters. Zearley et al. (2012) did not observe such acclimation for DCF biodegradation. This was attributed to the presence of microorganisms already acclimated to DCF (secondary substrate utilization) or capable of co-metabolism on aged biological sand filters. Such behavior was not observed in this study.

7.3.4 Impact of PAC age on MPs removal kinetics

The impact of increasing PAC age on the performance of the HMP depended on the MP monitored. In this section, the results in SW are presented. The impact of the water matrix will be presented in section 7.3.5. Both aged PACs exhibited a similar efficiency to that of virgin PAC when targeting a 1 Log removal. The t_{90} was 3 min or lower on aged PACs for all the MPs (see

Table 7-3). For ATZ, DEA and CAF, the 2 Log removal objective was more challenging on aged PAC. DEA was the most problematic compound as a 2 Log removal could not be reached by any of the aged PACs under realistic HMP contact times in SW (e.g. 30 minutes). As seen on Table 7-3, t_{99} for ATZ PAC was in the same order of magnitude (5-10 min) on 0-d and 10-d and >50 min on 60-d PAC, which is deemed a fairly long contact time for a full-scale application. For CAF, t_{99} was <3 min on 10-d PAC but >50 min on 10-d and 60-d PAC. Therefore, t_{99} varied along with PAC age as follows: 0-d ≤ 10-d ≤ 60-d. Yet, when applying a concentration of 1 g/L of 60-d PAC, the available adsorption capacity was sufficient to remove 95% of the initial concentration of each MP spiked within 5 minutes. The only study using aged PAC reported complete ATZ removal (MDL = 40 ng/L) from clarified water using 30-d PAC, which corresponds to a dosage of 11 mg/L (≈ 11 g PAC/L) at 20°C with an initial ATZ concentration of 0.5 µg/L and a contact time of 40 min (Lebeau et al., 1998). Direct comparison is difficult as both the MDL and the PAC concentration applied in their study were higher while the initial spiked ATZ concentration was 30 times lower than in the present study.

Figure 7-2 presents the effect of the PAC age on DEA and ATZ removal kinetics in SW. Similar curves were obtained for CAF. The adsorption rate decreased for ATZ, DEA and CAF when increasing the PAC age. This confirms previous observations while monitoring and modeling ATZ adsorption kinetics in presence of NOM on several aged PACs from an HMP (Lebeau et al., 1999). The aged PAC from this study is colonized by bacterial biomass (Stoquart et al., 2014a) and is pre-loaded by NOM from the SW. The presence of a biofilm might explain the hindered adsorption kinetics by a diffusion limitation (Fan et al., 1990). In GAC preloaded with NOM for 20 months, the film mass transfer coefficient was decreased due to NOM accumulated close to the GAC surface (Knappe, 1996). On PAC, pore blockage by the pre-loaded NOM could also reduce the adsorption kinetics by restricting the access and creating more complex paths towards the adsorption sites (Newcombe et al., 2002). Pore blockage was found to have serious impact on ATZ adsorption in systems such as the HMP, where the PAC is retained longer than the hydraulic retention time (Li et al., 2003b). Using PAC with larger pores, such as the one used in this study, can alleviate the pore blockage effect (Ding et al., 2008; Li et al., 2003b; Pelekani et al., 2000) as adsorption sites are more accessible than on microporous PAC (Newcombe et al., 2002). As a result, the mesoporous structure of the PAC used might have reduced the impact of

PAC aging on adsorption kinetics for contaminants spiked at high initial concentrations and presenting higher affinity for the PAC, such as MC or LIN.

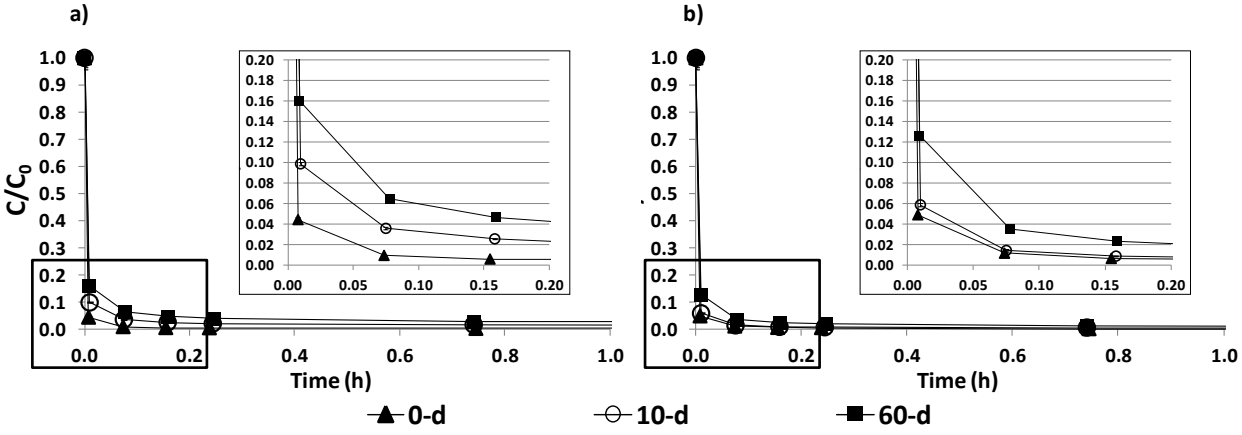


Figure 7-2 : Kinetics of removal of (a) DEA and (b) ATZ on 0-d (▲), 10-d (⊖) and 60-d (■) PAC in SW

In continuous flow systems such as HMPs, adsorption capacity is expected to decrease with increasing PAC age (Li et al., 2002). The pore blockage (Pelekani et al., 2000), the direct competition with small NOM (Li et al., 2003b) and the occupation of adsorption sites by pre-loaded compounds (Ding et al., 2008; Li et al., 2002; McDonough et al., 2008) or by soluble microbial products produced by the colonizing biomass (Zhao et al., 1999) were reported as being responsible for decreasing the adsorption capacity of the activated carbon. In contrast, at PAC doses of 4 mg/L and higher, it was shown that pore blockage by NOM might not affect ATZ adsorption equilibrium (Li et al., 2003b). In HMPs, Lebeau et al. (1999) attributed the hindering of the adsorption capacity to carbonate precipitation on PAC. However, since the Langelier index of the SW used to age the PAC in this study is highly negative, minimal calcium carbonate precipitation was expected on our PAC. In this study, adsorption capacities were only measurable for ATZ, DEA and CAF (on 60-d only), as all the other compounds were removed below MDL within 2 hours. PAC adsorption capacities for ATZ and DEA were similar (14.6 ± 0.6 µg/g) on the 3 PACs tested and CAF adsorption capacity might be reduced with PAC aging as CAF concentration was decreased below MDL on 0-d and 10-d PAC but not on 60-d PAC. The calculated ATZ adsorption capacity is inferior to the one reported for the same type of aged mesoporous PAC (62-d, 6 mg/g with an initial concentration of 10 µg ATZ/L) (Lebeau et al., 1999). However, this was calculated based on isotherms realized in presence of 150 µg ATZ/L,

which affects the adsorption capacity (Knappe et al., 1998). Yet, a loss in the adsorption capacity with PAC aging for ATZ and DEA cannot be ruled out. This issue cannot be completely addressed as adsorption capacities were calculated only once after a 6-hour contact time with a high PAC concentration.

7.3.5 Impact of the water matrix on the micropollutants removal kinetics

In this section, the impact of the water matrix was studied by comparing assays carried out in both SW and in pre-O_3 SW to evidence the competition between the NOM and the MPs for the adsorption sites. Ozonation is known to increase the BDOC to DOC ratio, decrease the aromaticity and size of the NOM and increase its hydrophilicity. Using the same PAC but altering the NOM by ozonation allows evidencing if competition for the adsorption sites significantly affects MPs removal under the conditions tested.

To estimate the impact of pre-O_3 on adsorption kinetics, t_{90} and t_{99} values obtained in SW and pre-O_3 SW were compared by calculating the ratio (R) between the t_{90} obtained in pre-O_3 SW and the t_{90} in SW for all the MPs; a similar ratio was calculated for the t_{99}. Average R-values were 1.3±1.1 for a 1 Log removal and 1.3±1.3 for a 2 Log removal (see Table 7-3). On 10-d PAC, lower R-values were calculated for CAF (R=0.03 on 10-d PAC) and DEA (R=0.1 on 10-d PAC). These R-values are considered to be outliers. Indeed, there was less than a 2% difference between the removals measured at the same contact time for both MPs. In conclusion, there was no major impact of using pre-O_3 SW instead of SW for all the MPs monitored on the 4 PACs investigated (paired t-test on R, $p = 0.47$). For the ATZ, DEA and CAF, an identical conclusion can be drawn for the calculated adsorption capacity (paired t-test on q_e, $p = 0.5$).

7.4 Discussion

A micropollutants' mixture was spiked at environmentally-relevant concentrations to demonstrate the potential of the HMP to remove MPs with aged PAC. For most MPs, the adsorption kinetics was extremely fast on the PACs tested. The abiotic assays carried out on 60-d PAC showed that biodegradation was not an important mechanism of removal. This was expected as a large fraction of the MPs was not biodegradable and the bacterial biomass colonizing PAC had not been acclimated to the biodegradable MPs (MC, CAF, DCF, PROG, MEDRO). In case of a continuous exposure of the PAC to MPs, the establishment of a specific biomass is likely to

occur, as observed in biological filters (Reungoat et al., 2011; Wang et al., 2007; Zearley et al., 2012). In that situation, the removal of the MPs amenable to biodegradation would result from the combination of adsorption and biodegradation.

In water treatment, Log D_{OW} (combining Log k_{OW} and pk_A) is a recommended indicator of the hydrophobicity of a chemical as it embodies the impact of pH (Wells, 2006). Concerning MPs spiked at the µg/L levels, ATZ, DEA and CAF were the most difficult to remove. They were the only contaminants detected after 48h (ATZ and DEA: MDL= 1 ng/L, CAF: MDL=7 ng/L) and 2 Log removals were not attained on 60-d PAC within reasonable HRT (30 min and less). CAF is the most hydrophilic compound tested (Log D_{OW} =-4), which justifies the lower adsorption efficiency. ATZ and DEA are neutral molecules with a low potential for either hydrophobic (Log D_{OW} =2.6 for ATZ and 1.5 for DEA) or electrostatic interactions. They were therefore less adsorbable and less competitive than the NOM. LIN was spiked at the same initial concentration as ATZ and DEA but the concentration was decreased below MDL (3 ng/L) within 15-45 minutes while ATZ and DEA were still detected after 48h (MDL: 1 ng/L). Log D_{OW} of LIN (3) is higher than that of ATZ or DEA, and its aromatic ring favors hydrophobic interactions with the graphite structure of the PAC, which explains the higher removal efficiency compared to ATZ and its derivate DEA. As for MC toxin, the analogues differ in molecular weight and hydrophobicity. No conclusion could be drawn as the spiked MCs were extracted from a *Microcystis aeruginosa* culture and MC analogues were not characterized. SMX, CBZ, DCF, PROG and MEDRO were spiked at the ng/L level. They were removed similarly with t_{99} values often being lower than 5 min. When compounds' concentration is at the ng/L level, characteristics such as the hydrophobic surface area (FOSA) and the compactness of the molecule relative to its molecular weight, depicted by the number of unique 8-bond path ($^{8}\chi_p$), were demonstrated as better indicators of the absorbability of MPs on activated carbons (Redding et al., 2009). However, under the operating conditions tested, all 5 MPs spiked at ng/L level were removed similarly. Therefore, the chemical characteristics of the MPs under study did not allow predicting the removals observed for these compounds.

Direct competition with NOM was not evidenced when substituting the SW water matrix with the pre-O_3 SW matrix. With 1 g/L of PAC, the availability of adsorption sites was not a limiting factor for the adsorption of most of the MPs monitored, as demonstrated by the rapid (within few minutes) complete adsorption of almost all the MPs. ATZ, DEA and CAF adsorption rates were

decreased with PAC aging, which confirms previous studies (Lebeau et al., 1999; Li et al., 2003b). The accumulation of NOM on the PAC retained in a carbon contactor has been shown to lead to pore blockage, subsequent decrease in surface diffusion coefficients and potentially adsorption capacity (Li et al., 2003b). However, no loss in adsorption capacity was observed in our study. Unlike in Li et al.'s study (Li et al., 2003b), the operation of our HMP pilot maintained a constant PAC age by using frequent PAC purge and feed. As a result, the aged PAC suspension used presented an age distribution, with a significant fraction of younger PAC providing a large amount of free adsorption sites (Stoquart et al., 2014b, Stoquart et al., Submitted). In the light of the high PAC concentration applied (1 g/L), it is suggested that the amount of younger PAC was most probably involved in maintaining the adsorption capacity. The usage of a mesoporous PAC might also have contributed to decrease the pore blockage rate of the PAC expected with aging (Li et al., 2003b).

The efficiency of the HMP for MPs removal might also be impacted by the following aspects. First, HMPs accumulate total suspended solids in their aged PAC suspension. These suspended solids are mostly composed of organic matter and aluminium salts microflocs (Léveillé et al., 2013). The binding of micropollutants with humic substances has been previously reported (Rav-Acha et al., 1992). Therefore, potential sorption of the MPs on suspended particulates and colloids could interfere with their adsorption on aged PAC (Darwano et al., 2014), especially if these colloids were to escape the carbon contactor. Secondly, the PAC used in this work had not been pre-exposed to MPs. The concentration of MPs originating from anthropogenic activities in source waters is expected to vary spatially and seasonally. A prolonged exposure to MPs could reduce the effectiveness of the HMP due to the displacement of adsorbed MPs by the continuous exposure to NOM of higher affinity for the adsorption sites (Li et al., 2002). Such displacement would be more likely to occur with aged PACs since the displacement rate increases at lower PAC dosage (Li et al., 2002). Finally, NOM and MPs are not targeting the same adsorption sites. The micropores favorable to the adsorption of MPs are not always occupied by the preloaded NOM. The extent of the loss in both adsorption capacity and adsorption rate depends on the molecular weight distribution of the NOM along with the pore size distribution of the PAC (Li et al., 2003b). Selecting the PAC with the proper pore size distribution is of major importance for optimizing the concomitant adsorption of NOM and MPs.

To conclude, if the HMP is operated with operating conditions optimized for ammonia or DOC (PAC concentration ranging from 1-40 g/L (Stoquart et al., 2012)), the process will most probably be effective to remove MPs present at sub µg/L levels. Adsorption kinetics was demonstrated to occur rapidly. If the HMP is operated at high HRT (30 min) with 1 g PAC/L (and higher), adsorption kinetics will not limit the treatment efficiency. However, if HRT is below 15 min, drastic differences in performances are expected and PAC age will have an important impact on process performance.

7.5 Conclusions

In presence of NOM, micropollutants spiked in settled waters at environmentally-relevant concentrations (from 130 ng/L to 33 µg/L) were rapidly adsorbed on aged PAC. On both virgin and aged PAC, removals of 95% of each of the micropollutants were attained within 5 min of contact time. Therefore, operating the HMP with a 1 g/L concentration of 10-d or 60-d PAC can control a transient MP pollution as the performance of the PAC contactor was sufficient to comply with the concentrations recommended by the World Health Organization for MC (1 µg/L) and ATZ (2 µg/L) even with 60-d PAC. However, the stricter European regulations for ATZ and DEA (0.1 µg/L) could not be met with 10-d and 60-d PAC under the operating conditions tested. Under prolonged exposure to micropollutants, the residual adsorption capacity of aged PAC would be reduced. Increasing the PAC concentration and reducing the PAC age would allow coping rapidly with peak events (as long as they can be detected).

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CHAPTER 8 GENERAL DISCUSSION

In this thesis, we sought to describe the performance of the HMP using aged PAC for drinking water production. Emphasis was put on the discrimination of the mechanisms responsible for the removal of the dissolved contaminants of interest with aged PAC. Such information is essential to enlarge our knowledge on aged PACs' management, and thus determine the key parameters and their relative importance for the operation of HMPs. This thesis provides crucial information for the establishment of operating guidelines of aged PAC suspensions in HMPs.

Figure 8-1 synthesizes the research work conducted over the course of this PhD.

The major strands of the present discussion are:

1. Methodological developments:
    - Quantification of the bacterial biomass on colonized PAC
    - Production of an abiotic control from colonized PAC
2. Dissolved contaminants removal in HMPs:
    - Removal kinetics monitoring
    - Identification of removal mechanisms on aged PAC
    - Key operating parameters for aged PAC contactors
3. Perspectives on the application of HMPs in the water industry

For each of these discussion themes, this chapter will highlight the main findings and discuss the limitations of this research project. We will conclude the general discussion by presenting the perspectives for the application of HMPs in the water industry.

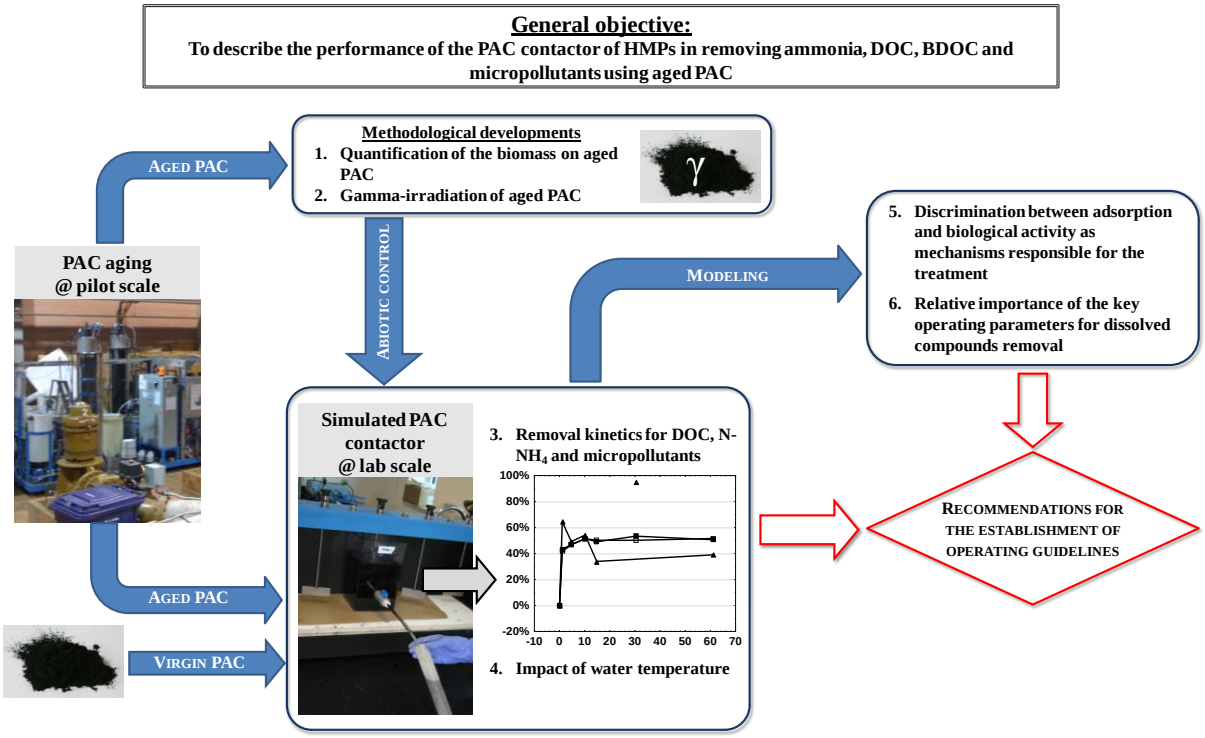

Figure 8-1 : Flowchart of the research conducted

8.1 Methodological developments

The first two specific objectives of this research project consisted in methodological developments deemed crucial for successfully achieving the rest of our research objectives. Indeed, as the operation of HMPs using aged PAC was investigated, the colonization of the PAC was expected. As mentioned in Chapter 1 (review), the published literature suggests that PAC aged from 20 to 30 days mostly works as a biological process, a situation where the nitrifying and heterotrophic bacteria are responsible for dissolved substances removal. The comparison of dissolved compounds removal on aged PAC and a corresponding abiotic control was the method chosen to evaluate the contribution of bacterial activity to observed removals. A biomass quantification method and a valid method to inhibit the biomass activity on colonized PAC were therefore necessary to achieve this objective.

8.1.1 Quantification of the bacterial biomass on colonized PAC

Most of the studies on HMPs using aged PAC suspensions were realized by monitoring dissolved compounds removals at pilot-scale with a PAC residence time higher than the hydraulic retention time (Chapter 1). Biological activity on aged PAC was evidenced by the increase in BDOC and ammonia removals with PAC aging (Léveillé et al., 2013; Markarian et al., 2010; Seo et al., 2004; Suzuki et al., 1998). However, until now, the extent of colonization of aged PACs was unknown as no method existed to quantify the bacterial biomass on PAC. On the other hand, several published methods were designed to quantify the biomass on colonized GAC from biological filters. However, for various reasons, many of these methods were not applicable to the case of biological PAC.

In this project, six of the methods developed for colonized GAC were adapted to colonized PAC. The greatest challenge faced during the shift from GAC to PAC is the superior residual adsorption capacity of PAC, which might interfere with some biomass quantification methods. Such interferences were noted when trying to estimate the heterotrophic biomass based on respirometry methods, as oxygen was adsorbed onto the PAC (Raev, 2010). In this research project, similar interferences were observed when trying to measure bacterial ATP as an indicator of the bacterial biomass. As the ATP released after the lysis of the bacterial membrane was immediately adsorbed by the PAC, the quantification based on ATP measurement was not successful. As suggested in Chapter 3, extracting the ATP directly from the sample would resolve the issue of ATP adsorption when evaluating the bacterial biomass onto the PAC. A novel technology integrating solvents extracts directly the ATP from the samples, this technology would be worth testing on aged PAC (e.g. LuminUltra© Deposit and Surface Analyses, LuminUltra Technologies Ltd., New Brunswick, Canada). The advantage of using ATP is the low cost, simplicity and speed of the analytical method while the disadvantage of the method is its absence of specificity to heterotrophic bacteria; indeed, all microorganisms contain ATP. However, it has also been extensively used to monitor bacterial biomass on biological GAC filters (Magic-Knezev et al., 2004; Niemi et al., 2009; Velten et al., 2011; Velten et al., 2007).

Five quantification methods were successfully adapted to aged PACs. Exopolymeric substances, EPS (i.e. proteins and exopolysaccharides), were extracted from the PAC samples but are not specific of heterotrophic bacteria as they include all types of bacteria and some other

microorganisms. Heterotrophic plate counts (HPC) quantify the abundance of culturable heterotrophic bacteria, but required to optimize the detachment of bacteria from the PAC. Indeed, an incomplete detachment of bacteria leads to an underestimation of biomass. These methods (HPC and EPS) were easily transferred to the case of colonized PAC. The potential glucose respiration (PGR) and potential nitrifying activity (PNA) measurements were the methods best adapted to the project's needs as they evaluate both the active heterotrophic and nitrifying biomass, which are the fraction of the biomass responsible for the biodegradation of NOM, and the nitrification of ammonia. The PAU method was developed as an alternative to the PGR method to alleviate the logistical and budgetary issues associated to the utilization of radio-labeled reactants.

In Chapter 3, 6 methods measuring the heterotrophic biomass were utilized on 4 different aged PACs and on biological GAC sampled at the surface of a biological GAC (BAC) filter. In Chapter 5, the PNA method was used on 10-d and 60-d PAC. The originality of this portion of the research project lays in the facts that i) Chapter 3 and Chapter 5 present the first quantifications of the heterotrophic and nitrifying biomass on aged PAC and ii) Chapter 3 is the first published comparison of methods quantifying the heterotrophic biomass on PACs. The first research hypothesis of this thesis was thus verified as significant heterotrophic and nitrifying bacterial biomasses were measured on 10-d and 60-d PACs. The active heterotrophic biomass in the aged PAC suspensions, expressed as PGR and PAU rates, increased with PAC aging (see Figure 3-2). In contrast, the measured active nitrifying biomasses, expressed as PNA, in 10-d and 60-d contactors from the Opaline® B pilot plant were similar (see Chapter 3). At first sight, such results are contradictory as nitrifying biomass growth is slower than that of heterotrophic biomass. The sensitivity to water temperature helps to explain these results. The heterotrophic biomass measurements were realized on PAC sampled during spring season, whilst the nitrifying biomass was measured on PAC sampled in winter. As the biomass activity decreases with lower water temperature, the season of sampling most probably impacted the results. Re-evaluating the heterotrophic and the nitrifying biomasses on colonized PAC and GAC samples would be of great interest. As both types of bacteria compete for the colonizing space, such measurements would provide further insight on the impact of operating conditions on the colonization of the PAC in HMPs. The investigation of microbial communities established on these PACs would

also be of great interest as different bacterial populations might be expected when comparing different PAC ages (Martiny et al., 2003).

In Chapter 3 and Chapter 5, the densities of both active heterotrophic and nitrifying biomasses (expressed per gram of dry PAC) were found comparable to that of the GAC from the surface of a BAC filter. Such comparisons must be considered with care. In HMPs, the activated carbon is a suspension considered homogenous (i.e. CSTR). Therefore, the colonization of the activated carbon (biomass density) is expected to be homogenous in the contactor. In contrast, BAC filters behave almost like plug flow reactors (i.e. PFTR), and the biomass density is rarely homogenous over the full depth of the BAC. As an example, nitrifying and heterotrophic biomass density is known to be higher at the surface of biological filters under summer conditions as the increased biological activity creates substrate limiting conditions at lower levels in the filter (Andersson et al., 2001; Servais et al., 1994). Therefore, if comparisons between biological filters and aged PAC contactors were done in the future, such stratification should be accounted for by sampling GAC across the whole depth of the filter. Total biomass available per liter of treated water should be compared instead of biomass per gram of activated carbon. This approach would enable to account for the differences in contact time and carbon concentrations within each type of process (i.e. filter vs HMP).

The results from the method developed herein (PAU) were highly correlated to the PGR rates. In Chapter 3, the PAU method is suggested as a suitable alternative to the PGR method for evaluating the active heterotrophic biomass. Nonetheless, the PAU method is less flexible than the PGR method as it requires having enough biomass (and thus enough colonized PAC) to discern a rapid decrease in the acetate concentration. Indeed, the precision of the method depends on the apparatus used while the PGR's can be improved by increasing the ^{14}C-glucose-to-non-labelled-glucose ratio in the reactant added. In addition, the protocol established for the PAU method is more applicable for PAC than GAC samples as this method requires the user to maintain a perfectly mixed 500 mL activated carbon suspension in order to collect representative samples and to keep the activated concentration untouched during sampling. Therefore, the applicability of the PAU method as developed herein is limited for GAC. The concept of the acetate uptake rate is valid and can be kept. The depletion of the acetate concentration should be monitored in synthetic water for both PAC and GAC, as per Stoquart et al. (2014a). Indeed, natural waters contain NOM, which is potentially amenable to biodegradation. Hence,

comparisons between PAU rates monitored in natural waters would not be possible due to the interference of the NOM competition. However, it is recommended to adapt the protocol of the PAU rate to GAC. In future research on GAC, using one reactor per contact time would be a potential alternative. This would avoid the problems associated to GAC concentration variation through time. Finally, the protocol of the PAU method should be refined by focusing the sampling process on the first hours of the acetate depletion monitoring in order to minimize the risk of a biomass increase, and to maintain the zero-order kinetic hypothesis. This will ensure that the acetate concentration is still superior to the Ks value on the time period used to calculate the PAU rate and that there is no deviation from linearity of the zero-order kinetic due to an increased heterotrophic biomass.

One of the limitations of the results presented in Chapter 3 and Chapter 5 is the small amount of samples tested. Validation of the adapted methods on a larger amount of samples (PACs and GACs) is therefore required. Yet, the measurements realized in this study provide a good basis for future quantifications. Amongst the methods proposed, using activity methods is recommended as it provides a better assessment of the biomass that will impact the removal of the compounds targeted. Amongst the methods of interest, the measurements of proteins were highly correlated with the heterotrophic activity methods. Measuring proteins on PAC samples thus appears as a cheaper and easier alternative for on-site evaluation of the colonization of the activated carbon.

8.1.2 Production of an abiotic control from colonized PAC

In BAC filters, adsorption and biodegradation are known as the predominant mechanisms responsible for the removal of NOM (Urfer et al., 1997) and other dissolved contaminants amenable to biodegradation such as microcystin (Wang et al., 2007) or MIB and geosmin (Persson et al., 2007). A similar behavior was expected in HMPs operated with high PAC residence times. To properly discriminate the relative importance of these two mechanisms, the main challenge was to find a method that produced an abiotic PAC control sample whose adsorptive behavior would be kept intact.

Gamma-irradiation was demonstrated as best suited for this type of study on soil samples (Berns et al., 2008), but it had never been tested on PAC. The second research hypothesis of this research project suggests the potential of the gamma-irradiation to produce an adequate abiotic

control for the removal kinetics monitored. To verify this hypothesis, an original protocol for the optimization of the gamma-ray dosage was established. Maximal admissible gamma-ray dosage was chosen based on methylene blue adsorption kinetics (Chapter 4). Alteration of the methylene blue adsorption kinetics was noted at high dosages (>15 kGy), it was therefore recommended to maintain the gamma-ray dose as low as possible. The determinination of the minimal dosage needed to inhibit the bacterial activity (10 kGy) was based on the inhibition of the culturability of the colonizing bacteria (HPC, as adapted to PAC in Chapter 3). Therefore, abiotic control was produced by sending a highly concentrated aged PAC suspension (50 g/L) to gamma-irradiation with a recommended dosage of 10 to 15 kGy. Refractory DOC (RDOC) adsorption kinetics and capacity on PAC were not impacted by the irradiation procedure (p-values: qe=0.63 and k =0.4, see Table 4-2). A residual bacterial activity of 17% of the initial PGR rates and 29% of the initial PAU rates was measured on the aged PAC sample exposed to the optimized dose of gamma-rays. Thus, the second hypothesis was verified as 83% of the heterotrophic bacterial activity (expressed as PGR) was inhibited in the samples. The residual heterotrophic bacterial activity measured on the abiotic samples is most probably due the following facts. Firstly, the HPC method used to determine the minimal gamma-ray dosage required provides an estimation of the biomass capable to grow on a culture medium. However, such method does not take into account the viable but non culturable bacteria (Oliver, 2005), which are part of the active biomass and could be responsible for the remaining bacterial activity on the abiotic samples. In spite of being more time consuming and expensive, using an activity based method such as the PGR or the PAU provides a better estimation of the minimal gamma-ray dosage required to inhibit the heterotrophic activity. Secondly, the highly concentrated PAC suspension most probably settles during the gamma-irradiation, which might lead to a heterogeneous exposure of the aged PAC during the gamma irradiation and thus to a remaining bacterial activity on the colonized PAC irradiated at the optimized dosage.

The application of the gamma-irradiation method to 10-d and 60-d samples successfully contributed to the discrimination of the mechanisms responsible for DOC and micropollutants removal in Chapter 6 and Chapter 7. In contrast, as the irradiation method was not optimized for nitrifying bacteria, it was not used in the context of discriminating ammonia adsorption from nitrification. Sensitivity of bacteria to gamma-irradiation is expected to vary (Thornley, 1963), therefore we anticipate that the optimized dose of gamma-ray differs from one species to another.

The efficiency of the method should therefore be validated for the nitrifying biomass and, in general, for each colonized sample under study as the bacterial population may vary from one site to another.

Finally, the gamma-irradiation method is costly, and requires an access to irradiating facilities close to the laboratory. Since the biomass activity could not be inhibited at a 100%, the period between the gamma-irradiation and the test should be minimized to make sure that biofilm is not altered and that the active biomass remains minimal. As gamma-irradiation is not available everywhere, further research should consider affordable alternatives. Sodium azide might interact with adsorbents (Chefetz et al., 2006), does not impact all bacteria equally (Lichstein et al., 1944) and might impact the ionic strength of the adsorption assay (Lotrario et al., 1995). Autoclaving was not our first choice as it affects the structure of exopolysaccharides (Berns et al., 2008) and impacts the adsorption characteristics of soils (Lotrario et al., 1995; Shaw et al., 1999). Nonetheless, soil samples and aged PAC differ in many ways and since sodium azide and autoclaving would be convenient alternatives, they would be worth investigating.

8.2 Dissolved compounds removal in hybrid membrane processes

There are already several full scale applications of HMPs (e.g. Vigneux, France, 55 MLD (Cristal®), L'Haÿ-les-Roses, France, 150 MLD (Opaline® S)), mainly in Europe where drinking water standards are more stringent. Indeed, the European Drinking Water Directive set the standard to 0.1 µg/L per pesticide, with a maximal total concentration of 0.5 µg/L; whereas the World Health Organization recommends the atrazine concentration to be below 2 µg/L. Most studies on HMPs confirm the great interest of coupling the usage of PAC with LPMs. The full-scale application of HMPs integrates PAC as an adsorbent that mainly targets the removal of NOM (i.e. DBPs precursors, BDOC) and trace organic contaminants (e.g. taste and odor compounds, algal toxins, herbicides,etc.). The process operated with virgin PAC is currently sold to treat groundwaters contaminated by trace contaminants, low turbidity surface waters with microbial contamination or as a polishing step. In case of highly contaminated source waters with taste and odor issues and a DOC of 4.2 mg C/L, Treguer et al. (2008) reported PAC dosages reaching 70 mg/L in a conventional treatment. Such high dosages were needed to overcome the competition between DOC and taste and odor compounds and to reach the targeted treatment objectives. As an alternative, they operated an HMP pilot-plant with a PAC residence time of 10

days, and reached the targeted removals with a PAC dosage three times lower. Reaching the treatment objectives with three times less PAC constitutes a substantial saving on operational expenses. HMP pilot plants using aged PAC were tested by Lebeau et al. (1998) and Treguer et al. (2010) as an intermediate step to treat clarified water, while Treguer et al. (2008) applied it directly on raw water. These studies gave encouraging results regarding the potential of HMPs using aged PAC to remove NOM and atrazine. Other studies evidenced the potential of this operating mode to remove ammonia (Seo et al., 2002; Seo et al., 2004; Suzuki et al., 1998). This section of the project fills in the gap evidenced in Chapter 1, namely the crucial lack of information regarding i) the performance of the HMP under critical conditions (i.e. low temperature, mixture of micropollutants and NOM) and ii) its optimization when using aged PAC. As HMPs are operated in continuous flow with a constant PAC dosage, adsorption equilibrium is most probably not reached in the contactor. Kinetics monitoring was thus needed as it provides fundamental information for i) confirming the suggested potential of HMPs using aged PAC, ii) discriminating adsorption from biological oxidation on aged PACs for the various dissolved compounds investigated and iii) modeling ammonia and DOC removal in PAC contactors. All of these were proven to be useful tools to get an improved understanding of aged PACs' behavior and provide sound recommendations for the optimization of the process and aged PAC management.

8.2.1 Removal kinetics monitoring

Monitoring removal kinetics of carbon, ammonia and micropollutants on aged PAC was an important portion of this thesis. The characterization of the removal kinetics occurring on a suspension of aged PAC withdrawn from an HMP pilot plant at steady-state was an original feature of this research project. While adsorption kinetics studies on virgin PAC are commonly found in the literature, only one published study investigated atrazine removal kinetics on aged PAC (Lebeau et al., 1999). The monitoring of ammonia, DOC and micropollutants removal kinetics with aged PAC representative of the full-scale application of HMPs was a first contribution.

The potential of HMPs using aged PAC to remove ammonia and NOM had been evidenced in the past by monitoring ammonia and DOC removals in pilot plants. The ammonia and DOC removal percentages found in Chapter 5 and Chapter 6 at 22°C both fall in the range reported in our

literature review (see Figure 1-4). Complete ammonia removal was attained in HMPs operated with aged PACs at 22°C. At 22°C, DOC removal in SW was approximately 80%, 44% and 25% on 0-d, 10-d and 60-d PAC, respectively. As mentioned in the literature, the DOC removal decreased while ammonia removal increased with PAC aging in Chapter 5 and Chapter 6.

The first original feature of the kinetics monitoring was the focus on the impact of water temperature on treatment efficiency. DOC removal efficiency followed temperature decreases on both virgin and aged PAC. Nevertheless, the efficiency of the process remained significant as 58%, 30% and 13% of DOC were removed at 7°C on 0-d, 10-d and 60-d PAC respectively. Interestingly, water temperature had contradictory effects on ammonia and DOC adsorption. Investigating the impact of water temperature on ammonia removal kinetics was of major interest, especially on aged PAC. Chapter 5 evidenced that 60-d PAC maintained a significantly higher ammonia removal at lower temperature than the 10-d PAC, which tends to confirm previous pilot scale observations (Léveillé et al., 2013). As an example, a 78% N-NH_4 removal was still attained at 7°C on 60-d PAC while no significant removal occurred on 10-d PAC. In Chapter 5, the total nitrifying biomass was demonstrated to be equivalent in both 10-d and 60-d reactors. However, the calculation of the PAC age distribution illustrates that 10-d and 60-d PAC age distributions contain biofilms of drastically different ages (Figure 5-1). It was hypothesized that these biofilms hosted different species of nitrifying biomass that were not distinguished by the PNA method. Therefore, in addition to the simultaneous estimation of the active heterotrophic and nitrifying biomass on aged PAC sampled, the investigation of the bacterial community composition in these aged PAC suspensions would allow us to confirm this hypothesis.

In order to properly characterize the DOC removal kinetics, RDOC and BDOC removal kinetics were also monitored. The distinction between RDOC and BDOC removals was an original feature of Chapter 6. Such monitoring was the first step towards the distinction of the adsorption and biodegradation of DOC as RDOC is removed by adsorption only, while BDOC could be both biodegraded and adsorbed. Interestingly enough, the kinetics evidenced that even though significant, the contact time had less impact on the performance outcome than for ammonia on aged PAC, as most of the removal occurred in the first minutes of contact time. In settled water, DOC was mainly adsorbed. Pre-ozonating the NOM might enhance the efficiency of HMPs by enhancing the biological activity through an increased NOM biodegradability (De Laat et al.,

1991). However, Treguer et al. (2010) highlighted that optimizing the ozone dose was difficult and that the increase in BDOC content might also lead to decreased adsorption efficiency. In the present study (Chapter 6), biodegradability of the NOM was increased but the pre-ozonation decreased the overall DOC removal efficiency, which is attributed to a decreased DOC adsorption that was not counteracted by a sufficient increased heterotrophic bacterial activity as observed by Léveillé et al. (2013).

Finally, Chapter 7 is the first study to demonstrate the potential of aged PAC to remove a mixture of micropollutants that differ in chemical characteristics and utilizations. Removals of 90% were reached on both 10-d and 60-d PAC within the first minutes of contact time (1 g/L of PAC at 22°C). Removals of 99% could not be reached for all the compounds investigated but at least 95% were removed within 5 minutes of contact time. The organic matter water matrix of the settled water was altered by pre-ozonation (0.85 g O_3/g C) as the BDOC-to-DOC ratio was increased. It is noteworthy that such alteration did not impact the removal kinetics of the micropollutants investigated. Under environmentally-representative concentrations of MPs, aged PAC concentrations of 1 g/L and higher can balance the potential direct competition of NOM for the adsorption sites.

When studying HMPs using aged PAC, the major challenge is to use aged PAC that is actually representative of the operating conditions expected in the industrial process. During this PhD research, the virgin PAC was aged at pilot-scale at a given concentration. The aged suspensions were sampled from this pilot plant, filtered and resuspended at lab-scale at the targeted concentration needed for the kinetics monitoring. This protocol was established to enable the comparison of the adsorption kinetics at various PAC concentrations. However, if the targeted compound is mainly biodegraded, the extent of the colonization should vary with the nutrient load, as observed in Chapter 5 for ammonia. Therefore, changing the PAC concentration at lab-scale might not be representative of the biomass expected under equivalent steady-state operation of the pilot. This limits the extent of the conclusions that can be drawn for the optimization of PAC concentration since adding various amounts of aged PAC in the reactors caused a variation in the biomass, which would not be the case at full-scale. In the case of a treatment based on adsorption, the extent of the pre-loading of the PAC will impact the observed removals. Therefore, the main limitation of the study presented in Chapter 7 lays in the fact that the aged PAC was colonized in SW with no significant micropollutant concentrations. The adsorption

sites of the aged PAC used were thus minimally preloaded with micropollutants. The observed efficiency of the HMP using aged PAC was a demonstration of the HMP's ability to face peak pollution rather than the demonstration of a sustained ability to face a continuous exposure to micropollutants. The same is true for the conclusions in Chapter 5 and Chapter 6, when monitoring the efficiency for ammonia removal in the matrix with a spiked ammonia concentration or when monitoring DOC removal in raw water or in pre-ozonated water. A more appropriate way to simulate PAC contactors at lab-scale would be to age the PAC in the pilot plant under the operating conditions that will be investigated at lab scale. However, such protocol is extremely complex to put into action as the variability in the quality of the feed water would require as many pilot plants as testing conditions to ensure the comparability of the aged PACs.

The method used to simulate the removal kinetics at lab-scale was highly reproducible, as kinetics monitored at a 1 year interval gave the same results. However, some improvements could enhance the quality of the results. The kinetic was monitored in a 2-L square beaker and samples of 100 mL were gathered at given contact times. In general, 0.5 L to 1 L was sampled in total over the monitoring of a given condition. Removing such an important fraction of the initial quantity of PAC might alter the concentration of the assay if the mixing is not perfect. In addition, using PAC concentrations representative of the full scale application of the HMP resulted in operating conditions where the PAC concentration was not a limiting factor for the removal of the dissolved compounds. Applying such high PAC concentrations was relevant as it demonstrated the performance of the process under operating conditions representative of the full scale operation of the process. As a downside, characterization of the adsorption kinetics was difficult as the maximal removal of the compounds monitored was reached within few minutes. Lower PAC concentrations are therefore recommended for that purpose. For example, Lebeau et al. (1999) applied a 12.5 mg/L PAC concentration. Concerning the comparison with virgin PAC, the 0-d PAC was pre-humidified and added at concentrations comprised between 1 and 10 g/L. Such an experimental plan allowed us to compare directly these kinetics with the ones monitored on aged PAC. However, net BDOC releases were evidenced when applying concentrations of 5 g/L and higher of 0-d PAC, which potentially reduced the maximal removal reachable on virgin PAC. Such BDOC release was not evidenced in previous studies as lower PAC concentrations and thorough cleaning of the PAC is usually done (Newcombe et al., 2002).

8.2.2 Identification of removal mechanisms on aged PAC

The results of this section are based on monitoring the ammonia, DOC and micropollutants kinetics. This section enables to validate or invalidate hypotheses #3, #4 and #6 of Chapter 2. These hypotheses focus on the mechanisms responsible for ammonia (#3), DOC (#4) and the mixture of micropollutants (#6) removals. Lebeau et al. (1999) evidenced the presence of a significant residual adsorption capacity on aged PAC (62-d) responsible for some atrazine removal. Unlike small molecules such as atrazine, the potential for NOM adsorption was not demonstrated in that study. Treguer (2007) confirmed the potential of 40-d PAC to adsorb atrazine and did a first attempt to distinguish the fraction of DOC adsorbed from the fraction biodegraded on 40-d PAC. In order to do so, DOC adsorption onto 40-d PAC was attributed to the fraction of virgin PAC dosed in the contactor to maintain a 40-d mean PAC age (12 g PAC/L). Adsorption on the aged fraction of PAC, which represented 99.9% of the total mass of PAC in the reactor, was neglected. Such hypothesis led to the conclusion that the observed increased BDOC removals associated to PAC aging were due to an increased biodegradation activity. However, artificial increases of the biomass did not lead to performance enhancements, which contradicts their conclusions. Treguer (2007) increased the PAC concentration with PAC age (from 4 to 12 g/L) to maintain equivalent virgin PAC concentrations (9.6±1.3 mg PAC/L) between the reactors. We suggest that adsorption on the older fractions of the 40-d PAC was responsible for the improved removal with PAC age, and not the bacterial biomass activity as suggested in his work. In Chapter 5 to Chapter 7, the proper discrimination of adsorption and biological oxidation was realized not only for DOC, but also for ammonia and a mixture of micropollutants. Hypothesis #6 was validated as the residual adsorption was demonstrated to be responsible for the MPs removal efficiency demonstrated in Chapter 7. This was expected as the aged PAC was non-acclimated to these micropollutants. The results obtained for ammonia and DOC were not expected, which is of major interest. They are the focus of this section of the general discussion.

Ammonia adsorption in PAC contactors has never been mentioned in HMPs' studies. In Chapter 5, significant ammonia adsorption was observed but complete ammonia removal was reached only on 10-d and 60-d PAC. Nitrification was therefore crucial to reach the complete ammonia removal. In Chapter 5, ammonia adsorption from SW was less than 10% with 1 g/L of 0-d PAC but reached 43% and 48% with 0-d PAC concentrations of 5 g/L and 10 g/L. Due to the low

fraction of 0-d PAC in 10-d and 60-d PAC suspensions (10% and 1.7% of the total mass), ammonia adsorption onto aged PAC was not expected to be significant. Based on nitrite and nitrates production, ammonia adsorption was demonstrated negligible on 10-d PAC and responsible for 10-25% ammonia removal on 60-d PAC. When exposing both aged PACs to a peak ammonia concentration, phosphate concentration is suggested as the limiting factor for nitrifying biomass activity. However, the residual adsorption capacity maintained a significant ammonia removal onto 10-d and 60-d PAC suspensions. Hypothesis #3 (ammonia adsorption onto PAC is hypothesized to be negligible) was therefore proven wrong as adsorption was responsible for removals of 10% and higher under most operating conditions.

In Chapter 6, hypothesis #4 was proven wrong as DOC biodegradation was not a significant contributor to DOC removal under the investigated colonizing conditions (BDOC concentration of 0.3 mg C/L in the feed water). A biomass density similar to that of BAC filters was measured (See Chapter 3). However, the original contribution of Chapter 6 is that adsorption was evidenced as mostly responsible for NOM removal.

In the present work, the biodegradability of the influent NOM affected the respective contribution of adsorption and biodegradation, which limits the conclusion that can be drawn on the relative importance of NOM adsorption and biodegradation. Due to the low BDOC content (0.3 mg C/L) of the settled water used to colonize the PAC, biodegradation did not play a significant role in NOM removal. When increasing the BDOC content in the water matrix, biological activity increased. It is expected that the relative importance of both mechanisms will vary from one study to another, which will impact the optimization of the process. Since biomass quantification methods were made available in Chapter 3, the optimization of the HMP would benefit from research focusing on the impact of the operating conditions on the colonization of the PAC. As an example, it was concluded in Chapter 6 that the PAC concentration was not a key operating parameter for DOC removal. However, this conclusion is restrained to the 1-10 g/L range, with a negligible amount of DOC biodegraded. In the case of a higher BDOC content in the feed water, a higher heterotrophic biomass is expected. Léveillé et al. (2013) observed an increased BDOC removal when pre-O_3 the feed water in their HMP pilot plant operated without PAC. Such increase was attributed to increased biomass in the accumulated suspended solids aged of 30-d. However, no significant impact was noticed when using 30-d PAC suspension in the pilot plant. Such a result is due to the opposite impact of ozonation on DOC biodegradability and

adsorbability (De Laat et al., 1991). Yet, if the BDOC content is naturally higher than that in the present study, the biomass will be increased, as suggested in Léveillé's pilot plant without PAC, and the adsorption kinetics along with the residual adsorption capacity of the aged PAC are likely to be impacted.

Finally, accumulated suspended solids in PAC contactors can represent 10-20% of the total mass of solids in a 60-d PAC suspension operated at a concentration of approximately 10 g/L and a HRT of 67 min (Léveillé, 2011). While no DOC adsorption was evidenced in the absence of PAC, the adsorption onto the suspended solids is likely to be responsible for some of the ammonia adsorption onto aged PAC suspensions evidenced in Chapter 5. In Chapter 7, adsorption of micropollutants onto the organic matter from the suspended solids was also suggested. The potential role of these suspended solids was not specifically measured in the present study. Future research on aged PAC suspensions should therefore integrate this aspect in their experimental plan. It is advised not only to discriminate adsorption from biodegradation but also adsorption onto PAC from adsorption onto the suspended solids as this will influence the optimization of the process.

8.2.3 Modeling ammonia and DOC removals

Modeling dissolved contaminants removals is possible either by developing statistical models, or by describing the mechanisms responsible for the removal of the targeted compounds in the process. Statistical models are based on empirical results. They are easier to develop but simplify the description of the mechanisms and are not based on theoretical reasoning. In contrast mechanistic models provide further insight on the mechanisms responsible for the kinetics monitored, with the drawback of a greater complexity. In the present study, mechanistic and statistical approaches were combined to describe ammonia and DOC removal in HMPs. Micropollutants removal was not modeled due to the limited data available.

For ammonia removal, nitrification was described by kinetics (i.e. Michaelis Menten kinetics) and the impact of the temperature was described by an Arrhenius law, which is an empirical relationship widely used for describing the influence of temperature onto reaction rates. Hypothesis #5 was therefore verified for nitrification as the Michaelis-Menten equation and Arrhenius law well described the nitrification kinetics monitored. Ammonia adsorption was based on the combination of pseudo-second order kinetics and Freundlich equilibrium, and the

impact of temperature was also described by an Arrhenius law. A statistical approach was used to adjust the parameters of the model developed.

For DOC removal, DOC biodegradation was not accounted for in the modeling as DOC biodegradation was not a major contributor to DOC removal under our test conditions. Therefore, hypothesis #5 could not be verified for DOC biodegradation. DOC adsorption was described based on mechanistic reasoning accounting for i) the loss in adsorption capacity with PAC age and ii) the PAC age distribution in aged PAC suspensions. Parameters were adjusted statistically.

The original contributions of the models developed herein are multiple. In Chapter 5, ammonia adsorption was accounted for in the modeling effort. Under low temperature conditions, this model evidenced that the increased ammonia adsorption could partially counteract the loss in nitrifying activity. However, the nitrifying activity was still crucial for complete ammonia removal. In Chapter 6, the model included the PAC age distributions in the prediction of the DOC adsorption. This innovative approach evidenced that in presence of marginal biodegradation, DOC is mostly adsorbed onto the youngest portion of the PAC distribution. Figure 6-5 illustrates this result well and highlights that the older fraction of the PAC age distribution can be put to contribution in case of a peak pollution event. However, the scope of application of the developed models is narrowed to high PAC concentrations. When describing ammonia adsorption, the PAC age could not be included in the modeling effort. In particular, ammonia adsorption in aged PAC suspensions is attributable to adsorption onto PAC but also suspected to be due to the presence of suspended solids, which should be the focus of subsequent research efforts. Ammonia adsorption was described with pseudo-second order kinetics, which is largely applied for the adsorption onto PAC. However, adsorption on suspended solids might be responsible for the non significance of the adsorption parameters and makes the case for additional research efforts around the role of suspended solids in such a process. When describing DOC removal in HMPs, the major limitation was the fact that DOC biodegradation was put aside in the modeling work. Such particular situation was related to the colonizing conditions in the Opaline® B pilot plant. Therefore, an additional term accounting for BDOC biodegradation should be added. Using a Michaelis Menten approach is suggested.

The homogenous surface diffusion model (HSDM) is a mechanistic model commonly used to simulate the adsorption onto activated carbon particles (Crittenden et al., 1978; Lebeau et al.,

1999; Najm, 1996). This model describes the diffusion of the compounds into the stagnant film layer, the adsorption onto the outer surface of the PAC and the surface diffusion towards the final adsorption sites. However, in order to use the HSDM, the experimental dataset should not include data points close to the equilibrium concentration (Najm, 1996). As mentioned earlier, the range of PAC concentrations tested during this research was designed to be representative of a full-scale application. However, when using representative PAC concentrations, ammonia and RDOC adsorption were almost immediate, as illustrated in Figure 5-2 and Figure 6-1. As a result, the usage of the HSDM was hindered by the experimental plan applied. As an example, Lebeau et al. (1999) successfully applied this model but batch kinetics had been monitored at a 12.5 mg/L concentration, which allowed to monitor significant changes of the dissolved compound concentration for a longer period of time. Still, the models developed during the present research project enabled to predict ammonia and DOC adsorption and contributed in the differentiation of ammonia adsorption and nitrification.

Several improvements to the developed models are therefore possible, especially when it comes to the description of the adsorption kinetics. Additional experiments could help define the values of the HDSM parameters and the model could be converted to a purely mechanistic model. In this case, it is recommended to monitor these kinetics on aged PAC with no age distribution. This would provide additional information on the impact of PAC aging on the adsorption kinetics. Performance could then be predicted based on the PAC age distribution, as done in Chapter 6. In general, developing a purely mechanistic model would be of great help for the design of the HMP, as suggested for the design of biological filters and the Chabrol model describing biodegradable organic matter removal (Billen et al., 1992; Laurent et al., 1999). For the daily management of the process or a thumb rule approach of design, simplified models based on large sets of data gathered from the full-scale operation of the HMP would be of interest, as per Huck et al. (1994) for biological filters.

8.2.4 Key operating parameters for aged PAC contactors

The interest in operating HMPs with aged PAC is mostly economical as it has potential to reduce the operating costs of the process. However, optimizing the operating parameters is required to reach the targeted drinking water quality.

8.2.4.1 Implications of the operating parameters on the drinking water quality

High removals of ammonia, DOC and micropollutants were evidenced on aged PAC. However, the performance of the HMP was affected by the PAC concentration, PAC age and hydraulic retention time (HRT). Up to now, the role of these operating parameters had been suggested but they had never been systematically investigated. As a result, there is little information available for the water industry to optimize the operation of HMPs using aged PAC. The main contribution of this research project is most probably the insight it brings on the management of aged PACs and the implications on the treated water quality of the major operating parameters that are the PAC age, PAC concentration and the HRT. Hypothesis #7 of Chapter 2 was verified as all three operating parameters influenced significantly the efficiency of the process.

During this project, it became clear that the usage of aged PACs of 10-d to 60-d was not as straightforward as it seemed, and that depending on the treatment objectives, the aged PAC could still be used as an adsorbent as well as a support for biological activities. As demonstrated, the majority of the ammonia removal occurs by nitrification under natural ammonia concentration, while ammonia adsorption onto aged PAC and suspended solids participates in an additional removal. However, optimizing ammonia removal through nitrification is recommended as the amount and the characteristics of the suspended solids in PAC contactors cannot be controlled, and their adsorption potential will vary greatly. In the present study, DOC and micropollutants were removed mainly by adsorption onto the aged PAC suspensions. The conclusions on the optimized operating conditions for DOC removal will be based on these conditions but the implications of higher BDOC content in the influent will also be discussed. In the following paragraphs, each of the operating parameters is discussed separately.

The PAC age is of major importance as it heavily impacts the quality of the treated water. The optimization of the PAC age will greatly vary depending on whether it is used more as a support for biological activities or as an adsorbent. In the case of DOC adsorption, using 10-d PAC allowed the removal of 50% of the DOC at 22°C and 30% at 7°C under colonizing conditions of 5 g PAC/L. Such results corresponded to DOC concentrations in the treated water of 1.4 mg C/L and 2.3 mgC/L, respectively. Under these conditions, ammonia removal was complete at 22°C and negligible at 7°C. Increasing the PAC age to 60-d PAC brought increased resilience to temperature change for ammonia removal as 78% removal was still reached on 60-d PAC. It

slowed down the micropollutants adsorption kinetics and decreased the DOC removals to 27% at 22°C and 22% at 7°C. Thus, when favoring the biomass activity, increasing the PAC age above 10-d was of interest. At pilot-scale, BDOC removals were not improved when increasing the PAC age from 30-d to 60-d (Léveillé et al., 2013). Therefore, when favoring biological activity, PAC age above 30-d might not improve the DOC removal. The interest of increasing the PAC age from 30-d to 60-d on ammonia removal is not reported. In contrast, when aged PAC is mostly used as an adsorbent, increasing the PAC age above 10-d should be taken with care as adsorption efficiency was demonstrated to decrease significantly. Furthermore, another drawback of using aged PAC as adsorbent is the potential displacement of adsorbed compounds. As an example, in case of a prolonged exposure to micropollutants, the adsorption sites of the older fraction of PAC will be loaded by these MPs. This older fraction will then be continuously exposed to NOM of higher affinity for the adsorption sites, which could displace the already adsorbed micropollutants and reduce the quality of the treated water (Li et al., 2002). In such situation, either the PAC age should be decreased or the aged PAC concentration should be increased in order to provide sufficient adsorption sites.

In general, when testing PAC concentrations comprised between 1 and 10 g/L, the PAC concentration did not appear limiting for the removal of ammonia and DOC. However, as the PAC was aged at a given concentration and then re-suspended to the targeted concentrations, impact of the PAC concentration on the process was biased. Indeed, PAC pre-loading and biomass density (per gram of activated carbon) were determined by the PAC concentration in the PAC contactor. It is therefore not possible to recommend a PAC concentration for the optimization of the process. However, the monitored kinetics provided novel information useful to the understanding of the implications of the PAC concentration on the efficiency of the process. For ammonia removal, as long as sufficient support is provided for the biomass growth, PAC concentration was not a concern in this study. During this research project, 10-d PAC was colonized at 5 g/L, which was demonstrated as a sufficient PAC concentration to reach complete ammonia removal. In the published literature, increasing the PAC concentration from 5 to 25 g/L was demonstrated to have marginal impact on BDOC removals but a drastic effect on ammonia removals when using the exact same PAC as in this study (Markarian et al., 2010). Yet, complete ammonia removal was never reached (Markarian et al., 2010). Major differences between that study and the present work were the HRT applied (15 min vs 60 min in this study) and the

porosity of the membrane use to retain the PAC in the contactor during colonization (ultrafiltration membrane vs a 10 µm sieve). Increasing HRT improved ammonia removal but complete removal was never reached. Therefore, comparing both studies demonstrates the importance of retaining the bacteria in the PAC contactor, either by maintaining sufficient support for attachment or physically using membranes. Under biological mode, providing sufficient PAC support was demonstrated as beneficial to the resistance of the process to water temperature changes (Léveillé et al., 2013). In contrast, DOC adsorption was demonstrated to mainly occur onto the younger fraction of the PAC. Sufficient overall PAC concentration is therefore required to provide sufficient PAC adsorption sites. While treating settled water, a PAC concentration between 1 and 5 g/L appeared sufficient. When increasing the PAC age, the minimal PAC concentration required to achieve a given treatment objective by adsorption is likely to increase since the portion of younger PAC in the age distribution is lower. This phenomenon will also be observed if NOM concentration in the influent increases, as the pre-loading of the older fractions of PAC age will be higher. As a result, increased performance will be needed from the younger fraction of the aged PAC distribution and higher PAC concentration could be required to ensure that there are enough adsorption sites available. As for micropollutants, the impact of the PAC concentration was not tested. Micropollutants removal kinetics were only monitored on 1 g/L of PAC. Almost all the compounds were removed below their respective MDLs. Since aged PAC concentrations in HMPs are expected to be higher than 1 g/L, the buffering capacity of the aged PAC suspension is expected to be sufficient to remove a large fraction of micropollutants. In case of a prolonged exposure to micropollutants, PAC concentration optimization and operation at a lower PAC age will most probably be required. As adsorption sites will be gradually loaded by MPs, competition between MPs and NOM for the remaining adsorption sites will be enhanced and the risk of displacement will be increased.

HRTs of 1 to 60 minutes were tested for ammonia, DOC and micropollutant removals. The largest fraction of DOC and micropollutants adsorption occurred within the first minutes of contact time. When adsorption is the principal mechanism, applying HRT superior to 15 minutes appears to be of minor interest. However, PAC aging was responsible for slowing down the atrazine, DEA and caffeine adsorption kinetics. This aspect should be considered with care and PAC age and concentration should be optimized accordingly. In contrast, nitrification was principally responsible for ammonia removal. The nutrient flux applied at pilot scale (HRT =67

min) determined the biomass present in the PAC contactor. As a result, an HRT of 60 min was required for complete ammonia removal. Increasing the nutrient flux would enable to increase the nitrifying biomass. Yet, HRT is largely known as a decisive parameter in the design of biological contactors (Servais et al., 1992; Urfer et al., 1997). Markarian et al. (2010) did not notice any improvement between HRTs of 30 and 60 min. The sensitivity of biological filters to the contact time for values ranging from 5 to 25 min is variable across the literature (Urfer et al., 1997). Such variations in the impact of the contact time in biological filters was attributed to variations in substrate (BDOC) content in the feed water, amount of biomass in the filter, types of filtration material and temperature (Urfer et al., 1997). In Chapter 5, an HRT of 15 min was recommended to begin with, as complete ammonia removal is reached in biological filters with EBCT of 10-15 min. However, additional tests would be required as PAC contactors and biological filters are not the same type of reactors and the lower efficiency of perfectly stirred reactors might require increased contact times. Furthermore, in the case of an increased nutrient load, PAC loading and colonization will be enhanced, and higher PAC concentration might be required.

8.2.4.2 Economic implications of the design and operating parameters

In this section, an analysis based on the calculation of the capital expenditure (CAPEX) and operational expenditure (OPEX) is provided to put into perspective the economic implications of operational versus design criteria. Globally, the optimization of aged PAC suspensions operation is based on the treated water quality targeted and the minimization of expenses. The calculation of the total cost of the HMP depending on the 3 operating parameters studied is presented herein for a design flow of 10 000 m^3/d and an average operating flow of 6 666 m^3/d (peak flow factor of 1.5). CAPEX was evaluated by considering the size of the PAC contactor while OPEX considered the amount of PAC used within the process. CAPEX is calculated by considering a cost of 1250$ per m³ of basin required and OPEX is estimated using a cost of virgin PAC of 2.25$/kg. Annual OPEX was actualized at a rate of 4% over 15 years. Total cost is given as the sum of CAPEX plus actualized OPEX such that: Total cost = CAPEX + 11.56*OPEX.

The impact of HRT on total cost of the process is illustrated in Figure 8-2 for a reactor operated with 5 g/L of PAC. The CAPEX of the HMP is directly proportional to the HRT, as the HRT determines the size of the PAC contactor required for a given design flow. OPEX is also dependent on HRT as the PAC dosage is proportional to it (see Eq. 1-2). From an economic

standpoint, it is crucial to minimize HRT. As HMPs with low PAC residence time operate at low HRT (15 min and less) and low PAC age and concentration, the economic viability of HMPs using aged PAC requires that the HRT remains in the same order of magnitude or that the increase in HRT be compensated by an increased PAC age. In the present research project, an HRT of 15 min appears as a relevant value to begin the optimization of the process. Indeed, DOC and MPs adsorption occurred within the first 5 to 10 minutes of contact time during the kinetics monitoring. Impact of such a low HRT on ammonia removal should be verified. In the case of decreased MPs adsorption kinetics with PAC age, a 15 minutes contact time removed most of the MPs, even on a 60-d PAC. Furthermore, decreasing the HRT from 60 min to 15 min was suggested when operating HMPs with aged PAC as for a given flowrate, the increased nutrient load would lead to an increased biomass in the PAC contactor. Increasing the HRT to values superior to 15 min should be strongly justified as it influences both the CAPEX and OPEX.

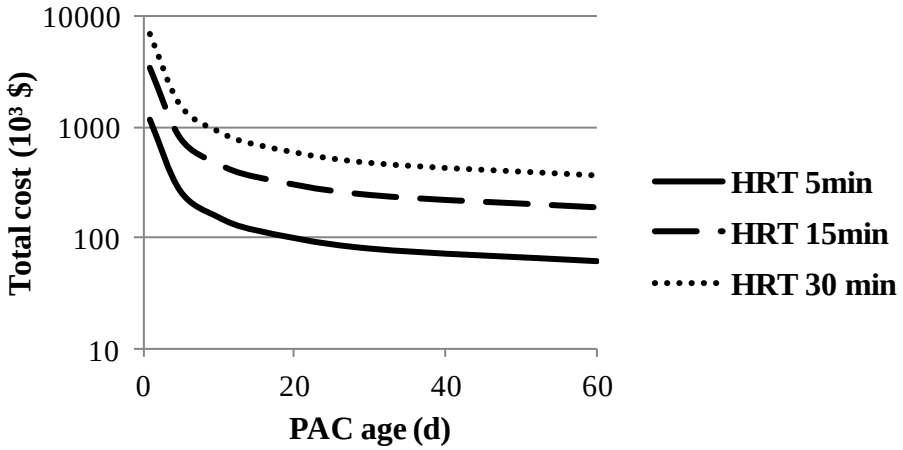

Figure 8-2: Impact of HRT on total cost in function of the PAC age at a PAC concentration of 5 g/L. Design flux is 10 000 m³/d and operating flux is 6666 m³/d.

Figure 8-2 also illustrates the significant economic interest of aging the PAC in HMPs. As illustrated, the economic interest in raising the PAC age is acute between 1-d and 20-d, at a PAC concentration of 5 g/L.

In Figure 8-3, the impact of the PAC age and PAC concentration on PAC dosage is illustrated. The PAC dosage is directly proportional to the OPEX and is used in Figure 8-3 to facilitate the comparison with dosages of PAC in conventional drinking water treatment. The applicability of HMPs in North America resides in the fact that PAC dosage should in our opinion be maintained

below 10 mg/L, whilst in Europe higher dosages are common due to the stricter regulations on MPs and DOC.

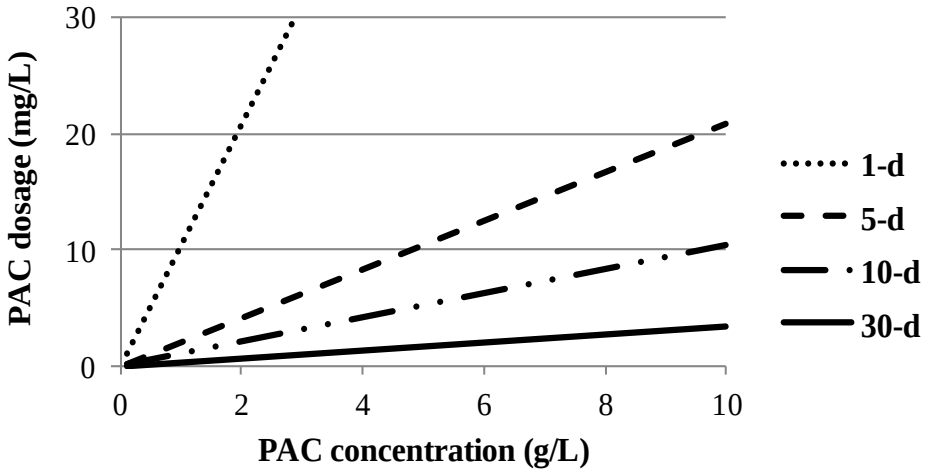

Figure 8-3: Impact of the PAC age and PAC concentration on the PAC dosage in a HMP with a 15 min HRT and treating a feed water flux of 6666 m³/d.

The optimization of the aged PAC suspension will be a balancing act between the PAC age and the PAC concentration required. Indeed, from our previous discussion, it is expected that when using aged PAC, higher PAC concentrations will be required to maintain sufficient adsorption capacity and kinetics. From Figure 8-3, it appears that there is little interest in increasing the PAC age from 5-d to 10-d if the PAC concentration has to be increased from 5 g/L to 10 g/L to reach the targeted treated water quality. This evidences the major difficulty that remains in the optimization of HMPs using aged PAC: optimizing both PAC age and concentration. As evidenced, the optimized operating conditions will vary greatly with the influent water and treatment objectives. Therefore, it is most probable that the optimization of HMPs using aged PAC will require an approach on a case-by-case basis. As illustrated, the major difficulty will reside in the fact that PAC aging will have to be pre-tested at pilot scale to define the design of PAC contactors.

From an economic standpoint, the HRT emerges as the first operating parameter to optimize. From a water quality standpoint, the three operating parameters appear to be intrinsically linked. If adsorption is the favored mechanism, increasing the dissolved compounds loading by decreasing the HRT for a given feed water flowrate will tend to increase the loading rate of PAC, which might lead to an increased PAC replenishment rate to maintain the process' efficiency. If

biodegradation is the mechanism favored, HRT optimization is a key parameter and its importance will decrease once sufficient biomass is present in the reactor. PAC age and concentration should be optimized simultaneously when adsorption is targeted. As PAC age affects drastically adsorption, it is a key operating parameter. Under a biological operating mode, higher PAC age will enhance the efficiency of the process and PAC concentration will be of less importance as long as sufficient support is provided. This will be of major importance, especially if nitrification is targeted as nitrifying bacteria growth rates are lower than that of heterotrophic bacteria, which make them less competitive if less support is provided.

8.2.4.3 Recommendations for the optimization of the design & operation of HMPs

The recommendations emerging from this work are an important step towards the optimization of the process. The models developed herein were extremely useful to get an acute understanding of the management of aged PAC. These models are too complex to be directly used by drinking water facilities for the on-line optimization of the process, as the parameters vary with the quality of the feed water and the colonizing conditions. In light of the complexity of PAC contactors optimization, an experimental approach is recommended to determine the optimized operating parameters of HMPs using aged PAC.

The first step towards optimization of HMPs using aged PAC is the characterization of the feed water and the determination of the treatment objectives. This will help to determine whether the HMP should be optimized with aged PAC used as an adsorbent only or both as an adsorbent and a support for biological activity. Typically, if ammonia removal is an objective, maintaining a biological activity into the PAC contactor should be considered. Higher HRT and PAC age with lower PAC concentration will be considered. If concomitant removal of NOM and MPs is targeted, HRT and PAC age should be lower than when only optimizing the biological activity. Increasing the PAC age will likely require increasing the PAC concentration. Based on the treatment goals set, the second step should be the choice of the adequate type of PAC used in the process. As an example, in presence of high NOM concentration, PACs having dual pore size distribution are recommended to maintain efficient MPs removal (Knappe et al., 1998). Adsorption equilibrium experiments and adsorption kinetics would help determine the PAC best adapted to the treatment needs. Once the adequate PAC is chosen, it is recommended to optimize the operating conditions during pilot scale tests using the following approach.

HRT is determined by the economics, the space available, the targeted performance and the priorities of the water facility. If a biological process is targeted, it is recommended to begin the assays with a HRT of 15 min at least. Yet, higher HRTs are likely to be required when temperature is decreased. If adsorption is targeted, lower HRTs might be applied depending on the compound targeted. First of all, the chosen PAC should be aged under several operating conditions. As initial value, HRT could be fixed to 15 min. The chosen PAC would be aged at least at three concentrations. During the PAC aging, dissolved compounds concentration should be monitored in the pilot plants. This would provide additional information about the impact of PAC aging on the efficiency of the process. The three pilot contactors would then be stabilized to the targeted PAC age with purges and dosages. Once steady-state results are gathered, the PAC age of the pilots could be raised and then stabilized again. Three PAC ages and three PAC concentrations would provide an idea of the optimal PAC and concentration required. When adsorption is the favored operating mode, the first PAC ages tested should be comprised between 5-d and 15-d. Indeed, an increase in the PAC concentration is likely needed when increasing the PAC age, which might diminish the interest of applying higher PAC ages. When biological oxidation is required, ages of 10-d to 60-d should be investigated, especially since Léveillé et al. (2013) did not notice any enhancement in BDOC removal above 30-d. Afterwards, influent flow rate could be raised or lowered depending on the importance of the biological activity for the treatment objectives to optimize the HRT. Such a pilot study should be done at different seasons to account for variations in water quality characteristics.

8.3 Perspectives on the application of HMPs in the water industry

Utilities using membranes will be required to meet new quality regulations on contaminants (e.g. pesticides, algal toxins, etc.) that cannot be removed with standard pressure or submerged MF/UF systems. In addition, given the large investments made in low-pressure membranes by drinking water facilities (450 MF/UF facilities were listed in 38 countries in 2005), finding innovative solutions is of paramount importance for them to achieve stricter standards. Hybrid membrane processes coupling PAC to low-pressure membranes are the perfect compromise: they are affordable, flexible, and meet the short-term challenges associated to micro-contaminants. Developing the operation of HMPs using aged PAC allows to reduce the costs and to broaden the spectrum of application of the Opaline® process. However, potential for this operating mode was

not completely known and additional information was required for the optimization of the process. The benefits of this thesis are important in several aspects. The potential of HMPs using aged PAC was further demonstrated, in particular at low temperature and for the removal of micropollutants. As micropollutants are a major focus for the drinking water industry, the demonstration of the potential of aged PAC suspensions for their removals is crucial for the wider usage of HMPs with aged PAC. This work also provides the first recommendations for the optimization of aged PAC contactors. Such recommendations are not only necessary for the full-scale application of HMPs with high PAC residence times, but also for any process that uses PAC. This project has therefore tremendous potential for direct application in Europe, where drastic pesticide regulations are effective.

CONCLUSIONS AND RECOMMENDATIONS

This research project resulted in the following conclusions regarding the monitoring of dissolved compounds removal kinetics by aged PAC suspensions in hybrid membrane processes:

- The monitoring of potential acetate uptake rates for the quantification of heterotrophic biomass is a promising alternative to the potential glucose respiration rate, a method using radio-labeled glucose and initially developed for biological GAC. Protein content was also highly correlated to heterotrophic bacterial activity and emerges as a good alternative to activity-based methods for on-site measurements of heterotrophic active biomass. ATP techniques could potentially be used but further method developments would be required to avoid ATP adsorption onto the PAC.
- The heterotrophic and nitrifying biomass density on aged PACs was similar to that of biological GAC sampled from the surface of a biological filter.
- The optimized gamma-irradiation of colonized PACs inhibited >80% of the heterotrophic activity on aged PAC without affecting dissolved organic carbon adsorption capacity and kinetics. However, gamma-rays have the potential to alter the adsorptive characteristics of the PAC at high doses. The sensitivity of the bacterial communities to the gamma rays is also expected to vary. The optimization of the irradiation dose is therefore case-sensitive and optimizing the dose is suggested for any new project intending to use this technique.
- Ammonia removal in HMPs can be as efficient as in biological filters. Ammonia adsorption on 60-d PAC is not negligible and allows to maintain a significant ammonia removal when the nitrifying bacterial activity is decreased at lower temperature. Even though adsorption was significant on 60-d PAC, nitrification remains crucial to the complete removal of ammonia at 22°C. Ammonia load was demonstrated as a limiting parameter for the growth of the nitrifying biomass under the investigated conditions. Phosphate limitation was suggested as the limiting factor to the nitrification in case of ammonia peak pollution.
- When aged in settled water with low biodegradable DOC content, adsorption was the main mechanism responsible for DOC removal. Biodegradation of DOC was not

significant. Pre-ozonating the water matrix decreased the overall efficiency of the process as adsorbability of the organic matter was decreased due to the ozone oxidation.

- The residual adsorption capacity evidenced on aged PAC for ammonia and DOC removal was also proven useful for the removal of a large variety of micropollutants. The HMP using aged PAC and operated to remove DOC and ammonia was efficient to control transient micropollutant pollution. Under prolonged exposure to micropollutants, the residual adsorption capacity of aged PAC would be reduced and operating conditions should be optimized accordingly.
- Integrating the description of ammonia and DOC adsorption in the modeling of the performance of HMPs using aged PAC is mandatory to accurately describe the performance of aged PAC suspensions. Accounting for the PAC age distribution demonstrated that in the case where adsorption is the major mechanism responsible for treatment, less than 35% of the mass of PAC is responsible for 80% of the DOC removal on 60-d PAC under the investigated conditions.

The literature review evidenced that HMPs using aged PAC were a promising alternative to conventional treatment but that these processes required to be optimized. The kinetics monitoring and modeling realized in this project provided original data that led to the following conclusions regarding the optimization of HMPs using aged PAC:

- Hydraulic retention time, PAC age and PAC concentration are operating parameters that will impact drastically the performance of the process. The optimized operating conditions of the PAC contactor of HMPs vary greatly with the characteristics of the feed water and with the treatment objectives. Therefore, operating parameters should be optimized seasonally.
- The hydraulic retention time has a major impact on the cost of the process as it impacts both capital and operational expenditures. It also significantly affects the efficiency of the process for the dissolved compounds whose concentration is decreased by bacterial activity. In the present study, the hydraulic retention time was set to approximately 1 hour in the pilot plant. Under these operating conditions, the ammonia flux was limiting the nitrifying biomass growth and high contact time was required to reach a maximal removal. In such a case, increasing the ammonia load was recommended by lowering the

hydraulic retention time towards values closer to that of biological filters (15 to 30 min). When dissolved compounds are mainly removed by adsorption onto aged PAC, the adsorption kinetics are generally faster than for biodegradation and the benefit of increasing the hydraulic retention time above 10-15 min appears limited.

- As long as sufficient support is provided, the PAC concentration is not a key operating parameter when biological oxidation is the favored mechanism for the removal of dissolved compounds. In the present study, there was no interest in increasing the PAC concentration from 5 to 10 g/L when optimizing ammonia removal.
- Increasing the PAC age improves the efficiency of HMPs under low temperature for ammonia removal. Significant ammonia removal (78%) was maintained at 7°C with 60-d PAC, while 10-d PAC was not efficient anymore (<10% removed). From this research, PAC ages comprised between 10-d and 60-d should be investigated first.
- When adsorption is the dominant treatment mechanism, the optimization of the PAC concentration is intrinsically related to the age of the PAC suspension. The younger fraction of the aged PAC suspension is responsible for the majority of the removal, and the amount of young PAC in the PAC age distribution decreases when mean PAC age is increased. As a result, using higher PAC age can be compensated by using higher PAC concentrations.

This research sought to answer the following questions: Does the residual adsorption capacity of aged PAC suspensions contribute significantly to the performance of the HMP for ammonia, DOC and micropollutants removal? Amongst the PAC age, the PAC concentration and the HRT, is there a key parameter in the operation of the HMP for ammonia, DOC and micropollutants removal? The results from our studies confirmed the major role that adsorption plays in the efficiency of dissolved compounds removal, even when operating HMPs with PAC residence times as high as 60 days. Whilst the ammonia concentration was mainly decreased thanks to the nitrifying bacterial activity under ambient conditions, the DOC and organic micropollutants were mostly adsorbed onto aged PAC suspensions. The residual adsorption capacity of the aged PAC was also proven useful to buffer peak pollution events of ammonia, DOC and micropollutants. The kinetics monitoring and modeling efforts evidenced that all three operating parameters of concern are interrelated. Yet, from an economic standpoint, hydraulic retention times of 15 min

or less are desirable to limit costs. The economic interest of increasing the PAC age can be attenuated by the potential increase in PAC concentration required if adsorption is the favored mechanism. Overall, a pilot-scale approach is recommended for the optimization of HMPs using aged PAC as the treatment objectives, the quality of the feed water and the fact that all three operating parameters are inter-related make the process optimization complex.

Additional research is needed on aged PAC contactors of HMPs. In this research, the operating conditions under which the PAC was aged were demonstrated as having a major impact on the findings of this project. The low BDOC content in the feed water of the process was a decisive factor influencing the outcome of this research. As a result, the biodegradation of the natural organic matter could not be accounted for. It is therefore recommended to pursue additional work on PAC aged in suspensions richer in biodegradable organic matter. Supplementary work should also characterize the adsorption kinetics and capacity of aged PAC. In this project, the demonstration of the potential of HMPs using aged PAC to remove micropollutants was of crucial importance, especially since micropollutants are emerging as an important concern for the drinking water industry. However, the observed performance demonstrated should be confirmed by future research with a variety of feed waters and micropollutants.

Minimizing the HRT is one of the priorities when optimizing the HMP using aged PAC as it influences both CAPEX and OPEX. In this thesis, it is recommended to apply a minimal HRT of 15 minutes in order to take advantage of both the adsorption process and the potential biological activity. Indeed, in biological filters, HRT of 10 to 15 min are sufficient for an optimized biological activity. Yet, biological filters and PAC suspensions are two different types of reactors. Biological filters behave more like plug flow reactors while the PAC suspension is more a perfectly mixed reactor. It is of primary importance to ensure the perfect mixing of PAC suspensions and to avoid dead zones in the reactor. This would allow to minimize the required HRT.

Previous research on the integrated HMP configuration evidenced abrasion issues that limited the applicability of the configuration. Therefore, the separated process is recommended until more resistant membranes are developed. The interest of the separated configuration also lays in the usage of pressurized membranes with higher operational fluxes. Still, the separated configuration requires at the moment a better separation system for the PAC. The Picahydro LP39 used in this

research might be too fine and create separation issues. Therefore, subsequent work is likely to use coarser granules such as the Picahydro L30-260 used in the Opaline S® Configuration. However, the adsorption kinetics are expected to be reduced with the increase in the median diameter of PAC grains. Therefore, the optimization of the operating parameters is expected to be largely impacted by the change in PAC size.

The increased pressure on fresh water supplies and the deterioration of source waters entail the development of advanced technologies to face the tightening of drinking water regulations. Powdered activated carbon and membrane filtration are amongst the most efficient technologies in drinking water treatment. Using aged PAC in HMPs is not only cost-effective but also a more sustainable approach of treatment.

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APPENDIX 1 : SUPPLEMENTAL INFORMATION, ARTICLE 1: HYBRID MEMBRANE PROCESSES USING ACTIVATED CARBON TREATMENT FOR DRINKING WATER : A REVIEW

Journal : Journal of Membrane Science

Title : Hybrid Membrane Processes Using Activated Carbon Treatment for Drinking water: a Review

Authors: Céline Stoquart, Pierre Servais, Pierre R. Bérubé, and Benoit Barbeau

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Table A-1. 1 : Published performances of the HMP with integrated activated carbon treatment: adsorption mode

Study	Scale	Raw water characteristics					Membranes			HRT (min)	Activated carbon				Performances (% removal)
		Water type	Pre-treatment	pH	T (°C)	TOC (mg/L)	Mate-rials	Pore size (µm)	Hydro-philic		Size (µm)	C_{PAC} (g/L)	D (mg/L)	Θ_{PAC} (d)	
Kim et al. (2007)	L	River water with secondary effluent	none	NA	23	1.6	NA	0.1	NA	NA	NA	4	none	0-2	Turb.: >96% TOC: 39% UV254: 68% SUVA: ~ 50%
												40		0-5	Turb.: >96% TOC: 83% UV254: 91% SUVA: ~50%
Lee et al. (2009)	L	Synthetic water (Has, kaolin in distilled water)	none	NA	20	NA	C	0.1	Y	NA	100-200	6	none	<1	Turb.: >99% UV254: >97%
Oh et al. (2007)	P	River water laden with sewage effluent	none	NA	NA	1-1.8 (DOC)	C	0.1	NA	120	151	20	none	0-7	Bacteria: below D.L. Virus: below D.L. DOC: 80% UV254: 90% THMFP: 81-89%
Saravia et al. (2008)	L	Diluted lake water, carbamazepin, clofibric acid, diclofenac and iohexol (10 µg/L each)	none	7	20	2.4 (DOC)	PES	0.1	NA	120	NA	0-0.04	10	0-2	Pharm.: >95% DOC: 55-64%
Song et al. (2009)	L	River water E2 (β-estradiol) (5-50 ng/L)	Prefiltra-tion on 0.45 µm	NA	25	NA	PE	0.4	Y	NA	20	NA	5	1	UV254: 26% E2: 92%
Zhao et al. (2005)	P	River water	Biofiltra-tion	NA	NA	NA	C	0.1	NA	58	36.5	20	none	0-7	Turb. : below D.L. DOC: 80%
											151				

HRT: Hydraulic Retention Time, L: Laboratory, P: Pilot, NA: Not Available, PES: Polyethersulfone, C: Ceramic, PE: Polyethylene, Y: Yes, D.L. : Detection Limit, Turb.: Turbidity, Pharm: Pharmaceutics

Table A-1. 2 : Published performances of the HMP with activated carbon pre-treatment: adsorption mode

Study	Scale	Raw water characteristics				Membranes				HRT (min)	Activated carbon					Performances (% removal)
		Water type	pH	T (°C)	TOC (mg/L)	Mate-rials	Type	MWCO (kDa)/ pore size (µm)	Hydro-philic		Size (µm)	C_{PAC} (mg/L)	D (mg/L)	Purge	Θ_{PAC} (d)	
Adham et al. (1991)	L	Ground water +TCP Pre-treated by greensand filter. + prefiltration on 200 µm	7.5	NA	3	CD	Pressurized hollow fiber, recirculation loop	100 kDA	Y	60	7-20	200	25	Y	<1	Turb. : <0.1 NTU TOC : ~ 45% UV254 : ~ 50%
Campinas et al. (2010)	L	Synthetic water with MC, HAs, TAs	NA	NA	NA	CA	hollow fiber, pressurized, inside-out, cross flow, recirculation loop	100 kDA	Y	60	6	Var	5 10	N	<1	MC : 70-84% (5 mg/L) 93-98-% (10 mg/L)
Campos et al. (1998)	L	Ground water + atrazine	7.3	NA	2.1 (DOC)	CD	hollow fiber, pressurized, inside-out, recirculation loop	100 kDA	Y	NA	10	0-288 0-576	4 8	N	<1	Atrazine : 30% (4 mg/L) 52% (8 mg/L)
												288 576	none			Atrazine: 51% (288 mg/L) 75% (576 mg/L)
Jacangelo et al. (1995)	P	River water, Prefiltered on 200 µm	7.8 7.9 7.6	NA	1.4 5.2 7.4	CD	hollow fiber, pressurized, crossflow, recirculation loop	100 kDA	Y	NA	Calgon WPH	Var	0-90 0-200 10	N	NA	TOC: 12-80% SDSTHM/TOX: 30-85% TOC : 22-55% TOC : 17% SDSTOX : 27%
Kim et al. (2008)	L	Lake water	7.6	20	2.4 (DOC)	CE	Flat sheet, pressurized, dead end	0.025 µm	Y	120	33.9	200	none	N	<1	DOC: >80% UV254: >90%
Mozia et al. (2004)	L	Lake water	6.5 8.7	NA	8.7-8.6	PAN	flat sheet, pressurized, cross flow, recirculation loop	110 kDA	Y	NA	10-50	NA	100	Y	<1	Color : 92% TOC : 56% UV254 : 64%

HRT: Hydraulic Retention Time, L : Laboratory, P.: Pilot, NA: Not Available, CD: Cellulose derivative, CA: Cellulose acetate, CE: Cellulose esters ,PAN: Polyacrylonitrile, Var : Variable, MC: Microcystin, Turb.: Turbidity, Y: Yes, N: No

Table A-1. 3 : Published performances of the HMP with activated carbon pre-treatment: adsorption mode (continue)

Study	Scale	Raw water characteristics				Membranes				HRT (min)	Activated carbon					Performances (% removal)
		Water type	pH	T (°C)	TOC (mg/L)	Mate-rials	Type	MWCO (kDa)/ pore size (µm)	Hydro-phylic		Size (µm)	C_{PAC} (mg/L)	D (mg/L)	Purge	Θ_{PAC} (d)	
Mozia et al. (2005)	L	Synthetic water with Has and phenols	5.7-6	NA	4.5 (DOC)	PSF	flat sheet, pressurized, crossflow, recycle loop	70 kDA	N	NA	10-50	NA	100	Y	<1	Color : >98% DOC : >98% Phenols : 100%
						CA		40 kDA	Y							
						PAN		110 kDA	Y							
Mozia et al. (2006)	L	Synthetic water with HAs and phenols, Pre-ozonated or not	5.7-6	NA	4.8 (DOC)	RC	flat sheet, pressurized, cross flow, recycle loop	30 kDA	Y	NA	10-50	NA	100	Y	<1	<u>Without ozonation:</u> TOC : 98% UV254 : 100% <u>With ozonation:</u> TOC : 100% UV254 : 100%
Pirbazari et al. (1992)	L	Surface water + TCE, HAs	NA	NA	9 (DOC)	C	tubular, cross flow, recycle loop	0.2 µm	Y	300	<44	2000-3000	50	Y	3-5	DOC: >60% TCE: >99.8%
Tomaszewska et al. (2002)	L	Distilled water + Phenols + HAs	6.7	NA	NA	PVDF	flat sheet, pressurized, cross flow, recycle loop	70 kDA	N	NA	10-50	Var	50-100	Y	<1	Color : 96% HAs : 89% phénols : 95% (50 mg/L) 100% (100 mg/L)
Tsujimoto et al. (1998)	P	Municipal water supply system	NA	NA	NA	PSF	Hollow fiber, Submerged, Outside-in	1 µm	NA	20	GAC filter					Bacteria: 100% Turb.: <0,2 NTU UV254: 60%
Xia et al. (2007)	P	River water	NA	NA	9.3 (DOC)	PVC	hollow fiber, pressurized, inside-out, cross flow, recycle loop	80 kDA	NA	NA	NA	Var	30	Y	<1	Turb.: >99% DOC: 46% UV254: 57%

HRT: Hydraulic Retention Time, L: Laboratory, P: Pilot, NA: Not Available, C : Ceramic, RC: Regenerated cellulose, CA: Cellulose acetate,PAN: Polyacrylonitrile, PVC: polyvinyl chloride, PVDF: poly(vinylidenefluoride), PSF: polysulfone , Has: Humic acids, Turb.: Turbidity, Y: Yes

Table A-1. 4 : Published performances of the HMP with integrated activated carbon treatment: biological mode

Study	Scale	Raw water characteristics					Membranes			HRT (min)	Activated carbon					Performances (% removal)
		Water type	Pre-treatment	pH	T (°C)	TOC (mg/L)	Mate-rials	MWCO (kDa)/ pore size (µm)	Hydro-philic		Size (µm)	C_{PAC} (g/L)	D (mg/L)	Θ_{PAC} (d)	Mode	
Khan et al. (2009)	L	Low quality river water	Sedimen-tation	NA	20-25	1.65	PE	0,1 µm	Y	288	NA	40	none	0-60	Ads & Biol	Average values TOC: 76 to 85% SUVA: ~ 90% THMFP: 80 to 95% (Cl-) 65 to 85% (Br-)
			Sedimen-tation + biofiltration			1.56										
Kim et al. (2009)	L	River water	none	7.62-8.02	8-15	2.7-3.2 (DOC)	PO	0,22 µm	NA	NA	GAC: 0.42-1.7 mm	1.5	replace-ment	0-70	Ads -> Biol	MP: 100% Turb.: 100% DOC: 46% -> 11% UV254: 95% ->25% SUVA: 62% -> 15%
Lebeau et al. (1998)	P	River water + NH_4Cl (0.6 mg N/L), atrazine (0.5 µg/L)	clarification	NA	20	2	NA	200 kDa	NA	43	NA	5-20	11	30	Biol	MP: > 99% Turb.: 97.5 % TOC: 50% DOC: 41% BDOC: 25% Atrazine: >92% ammonia: 98% nitrite: 50% Fe: >76 % Mn: 13% Al: 90%
			screened-raw with in-line coag.	7.05	8.5	3.4				72			12	60		MP: >99% Turb: >99% DOC: 69% BDOC: 86% Atrazine: >95% ammonia: >93% nitrite: 50% Fe: 93% Mn: >74% Al 93%

HRT: Hydraulic Retention Time, L: Laboratory, P: Pilot, PE: Polyethylene, PO: Polyolefin, NA: Non Available, Ads: Adsorption, Biol: Biological, MP: Microparticles, Turb.: Turbidity

Table A-1. 5 : Published performances of the HMP with integrated activated carbon treatment: biological mode (continue)

Study	Scale	Raw water characteristics					Membranes			HRT (min)	Activated carbon					Performances (% removal)
		Water type	Pretreatment	pH	T (°C)	TOC (mg/L)	Mate-rials	Pore size (µm)	Hydro-philic		Size (µm)	C_{PAC} (g/L)	D (mg/L)	Θ_{PAC} (d)	Mode	
Markarian et al. (2010)	L	River water	conventional treatment + post-ozonation	6.67	10.3-12.3	2.93 (DOC)	10 µm nylon sieve			15-60	25-200	5 25	none	0-161	Ads -> Biol	<u>5 g/L reactors:</u> DOC: 10 -> 5% BDOC: -20 -> 30% ammonia: 0 -> 20% <u>25 g/L reactor:</u> DOC: 20-25 -> 7.5% BDOC: 0 -> 40-45% ammonia: 0-> 95% <u>30 d reactor:</u> DOC: 17% BDOC: 34% ammonia: 50% <u>HRT 15 -> 30 min:</u> BDOC: 34 -> 42% (5g/L) 51 -> 57% (25g/L) Ammonia: 5 -> 54% (5g/L) 83 -> 94% (25g/L)
											200	25	8.5	30	Ads & Biol	
Seo et al. (2002)	L	River water + NH_4Cl (10 mg/L)	NA	NA	2-25	NA	NA	0.1	NA	NA	PAC	40	none	0-250	Biol	Ammonia: 100% (25°C) 100% (10°C) 75 -> 100% (4°C) 100% (2°C)
Seo et al. (2004)	P	River water + DBPs, NH_4Cl (1-7 mg/L)	clarification + rapid sand filtration	6.5-7.2	2-30	1.53-2.83 (DOC)	NA	0.1 0.4	NA	NA	NA	20-40	none	0-90	Ads -> Biol	DOC: 80% -> 30-40% UV254: 95% -> 40-50% HAAs: 92.1% THMs: 86.1% ammonia: >95% once acclimated

HRT: Hydraulic Retention Time, L : Laboratory, P: Pilot, NA: Not Available, PES: Polyethersulfone, Y: Yes, Ads: Adsorption, Biol: Biological, Turb.: Turbidity

Table A-1. 6 : Published performances of the HMP with integrated activated carbon treatment: biological mode (continue)

Study	Scale	Raw water characteristics					Membrane			HRT (min)	Activated carbon					Performances (% removal)
		Water type	Pretreatment	pH	T (°C)	TOC (mg/L)	Mate-rials	Pore size (µm)	Hydro-philic		Size (µm)	C_{PAC} (g/L)	D (mg/L)	Θ_{PAC} (d)	Mode	
Treguer et al. (2008)	P	water from Eagle Creek reservoir	none	NA	11-26	4.8-6	PES	NA	NA	120	Pica MP23	4.2	10	40	Biol	Turb: below D.L. DOC: around 20% (~0,8 mgC/L) T&O: 45-75% (40d) 70-80% (10d)
												1.05	10	10		
Treguer et al. (2010)	P	River water	clarification	6.3-6.8	NA	2.3-3,2	NA	NA	Y	40	Pica MP23	12	Var	40	Biol	DOC: 16-23% (0,4 mgC/L) BDOC: ~50% (0,5 mgC/L)
			clarification + ozonation													DOC: 19-28% (0,5 mgC/L) BDOC: ~50% (0,6 mgC/L)

HRT: Hydraulic Retention Time, P: Pilot, PES: Polyethersulfone, NA: Non Available, Y: Yes, Biol: Biological, Turb.: Turbidity, DL: detection Limit

Table A-1.7 : Published performances of the HMP with activated carbon pre-treatment: biological mode

Study	Scale	Raw water characteristics				Membranes					HRT (min)	PAC						Performances (% removal)
		Water type	pH	T (°C)	TOC (mg/L)	Mate-rials	Recirculation loop	Type	MWCO (kDa)/ pore size (µm)	Hydro-philic		Size (µm)	C_{PAC} (g/L)	D (mg/L)	Θ_{PAC} (d)	Purge	Mode	
Suzuki et al. (1998)	P	River water rich in Has	NA	3.5-25	3.35	PE	Y	Subm	0.1 µm	Y	10-15	NA	2-10	Var	0-45	Y	Ads ->Biol	At 18°C: TOC: 4% UV260: 69% ammonia: >99% Mn: >94% At T<5°C: ammonia: 60-70% Mn : decreases
Andersson et al. (2001)	P	River water	NA	NA	2.4 (DOC)	CA	N	Subm	150 kDa	Y	NA	GAC filter					Biol.	Turb: 100% Color: 89% DOC: 29% UV254:20% THMFP: 19%
Watanabe et al. (2000)	P	River water	NA	NA	3.36	PE	Y	Subm	0.1 µm	Y	10-15	NA	NA	Var	0-40	Y	Biol	TOC: ~45% UV260: ~70% ammonia: >95% Mn: >85%
Williams et al. (2007)	B-Sc	Ozonated Surface water with microbial inoculum (45 or 80 mg/L)	8	20	2.9-3	C	Y	Press	0.2 µm	Y	NA	<44	3	none	0-10	N	Biol	DOC : 90 -> 30% AOC : >98% THMFP : 99 - >15%
													<3	none	1-4	Y		DOC: 25-30% AOC : >98% THMFP : 15-40%
													Var	5	Var	N		DOC : 10-30% AOC : 98% THMFP : 20%
													Var	5	Var	Y		DOC : 35% AOC : >99% THMFP : 25%

HRT: Hydraulic Retention Time, B-Sc : Bench-Scale, P: Pilot, NA: Not Available, PO: Polyolefin, C: Ceramic, CA: Cellulose acetate, PE: Polyethylene, Ads: Adsorption, Biol.: Biological, Turb.: Turbidity, Subm: Submerged, Press: Pressurized, Y: Yes, N: No, Var: Variable

Table A-1.8 : Published performances of the HMP with activated carbon post-treatment: adsorption and biological modes

Study	Scale	Raw water characteristics				Membrane				Activated carbon	Mode	Performances (% removal)
		Water type	pH	T (°C)	TOC (mg/L)	Materials	Type	MWCO (kDa)/ pore size (µm)	Hydro-philic			
Schlichter et al. (2004)	P	River water, Prefiltered. on 21 µm, ozonated	6.9-7.6	2-9.2	5.2-12	PVDF	capillary, inside-out	NA	Y	BAC filter EBCT 6,9 min	Biol	Turb.: below 0.05 NTU Colif.: 100% Color: below D.L. TOC: 38.5% DOC: 31.4% UV254: 88.9% THM: 50% (below 80 µg/L) Nitrogen comp: Below D.L. Mn: below D.L.
Niquette et al. (2007)	P	Surface Water, Prefiltered on 50 µm, ozonated	7.2	NA	12.1	C	Multi-channel, Flat sheet, submerged	UF: 80 nm MF: 0.2µm	NA	GAC filter	Ads	Turb: >95% Color: >98% TOC: >87%
Suffet et al. (1980)	P	Concentrated River water, Prefiltered on 50 µm, ozonated	NA	20	3.9	C	tubular, cross flow, recirculation loop	20 kDa	NA	GAC filter	Ads + Biol	No germs detected. Turb.: >99% AOX: >55% TOC: >88% UV254: >94% Atrazine: below D.L.

HRT: Hydraulic Retention Time, P: Pilot, C: Ceramic, PVDF: poly(vinylidenefluoride), NA: Not Available, Ads: Adsorption, Biol: Biological, Turb.: Turbidity, Colif: Coliforms, Y: Yes, Var: Variable, DL: Detection Limit, EBCT: Empty Bed Contact Time

APPENDIX 2 : SUPPLEMENTAL INFORMATION, ARTICLE 2 : GAMMA IRRADIATION : A METHOD TO PRODUCE AN ABIOTIC CONTROL FOR BIOLOGICAL ACTIVATED CARBON

Journal : Environmental Technology

Title : Gamma Irradiation: A Method to Produce an Abiotic Control for Biological Activated Carbon

Authors: Céline Stoquart, Gabriela A. Vázquez-Rodríguez, Pierre Servais, and Benoit Barbeau

Number of pages: 1

Number of figures: 1

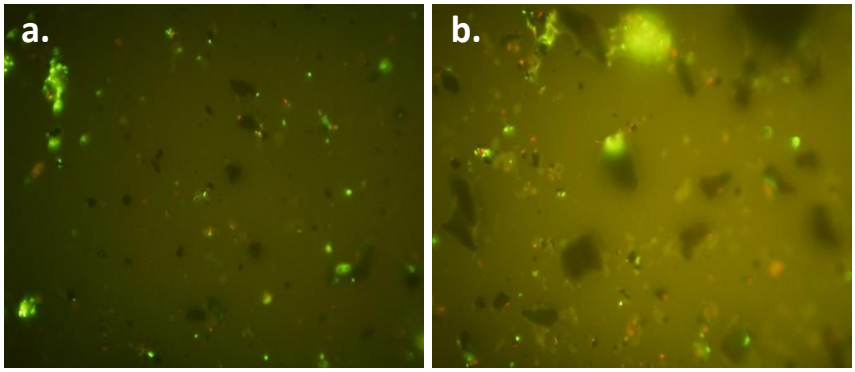

Figure A-2.1 : Impact of gamma rays (dose of 15 kGy) on the biofilm developed at the surface of colonized 60-d PAC. Comparison of *Bac*Light™ images of non-irradiated colonized PAC (a) and irradiated colonized PAC (b).

APPENDIX 3 : SUPPLEMENTAL INFORMATION, ARTICLE 5: DISSOLVED ORGANIC CARBON REMOVAL USING AGED POWDER ACTIVATED CARBON IN A HYBRID MEMBRANE PROCESS

Journal : Water Research

Title : Dissolved Organic Carbon Removal Using Aged Powder Activated Carbon in a Hybrid Membrane Process

Authors: Céline Stoquart, Pierre Servais and Benoit Barbeau

Number of pages: 6

Number of figures: 6

Number of table: 0

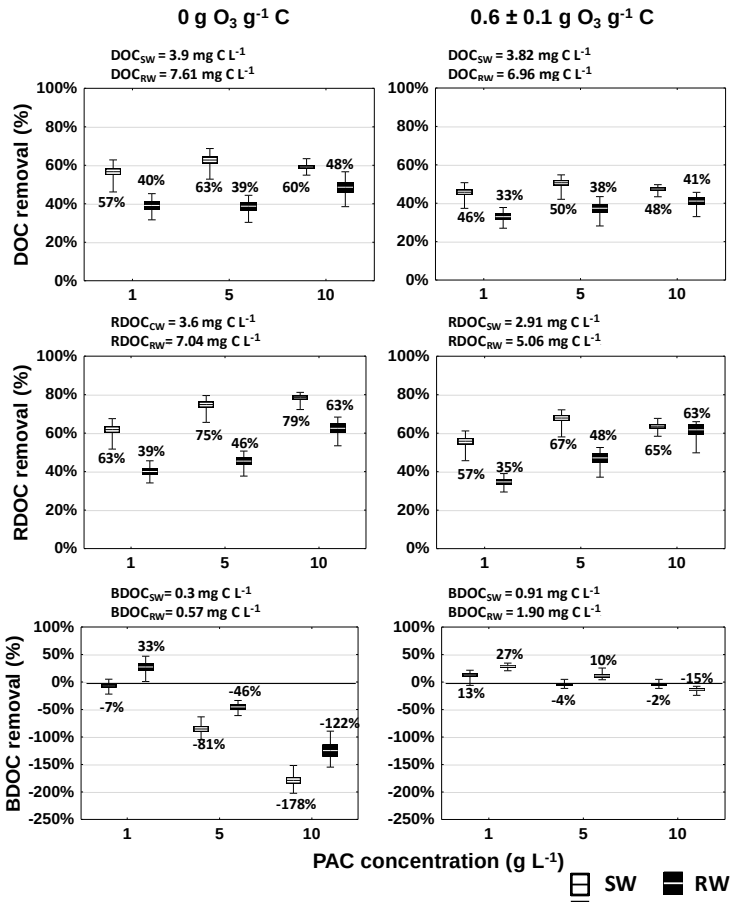

Figure A-3. 1 : DOC, BDOC and RDOC removals (in %, initial concentration presented above each graph) on virgin PAC at 7°C. The PAC concentrations were approximately 1, 5 and 10 g L^{-1}, and the water matrices were SW, pre-O_3 SW, RW and pre-O_3 RW. The boxes represent the mean removal ± the standard error, and the whiskers correspond to the minimal and maximal removals.

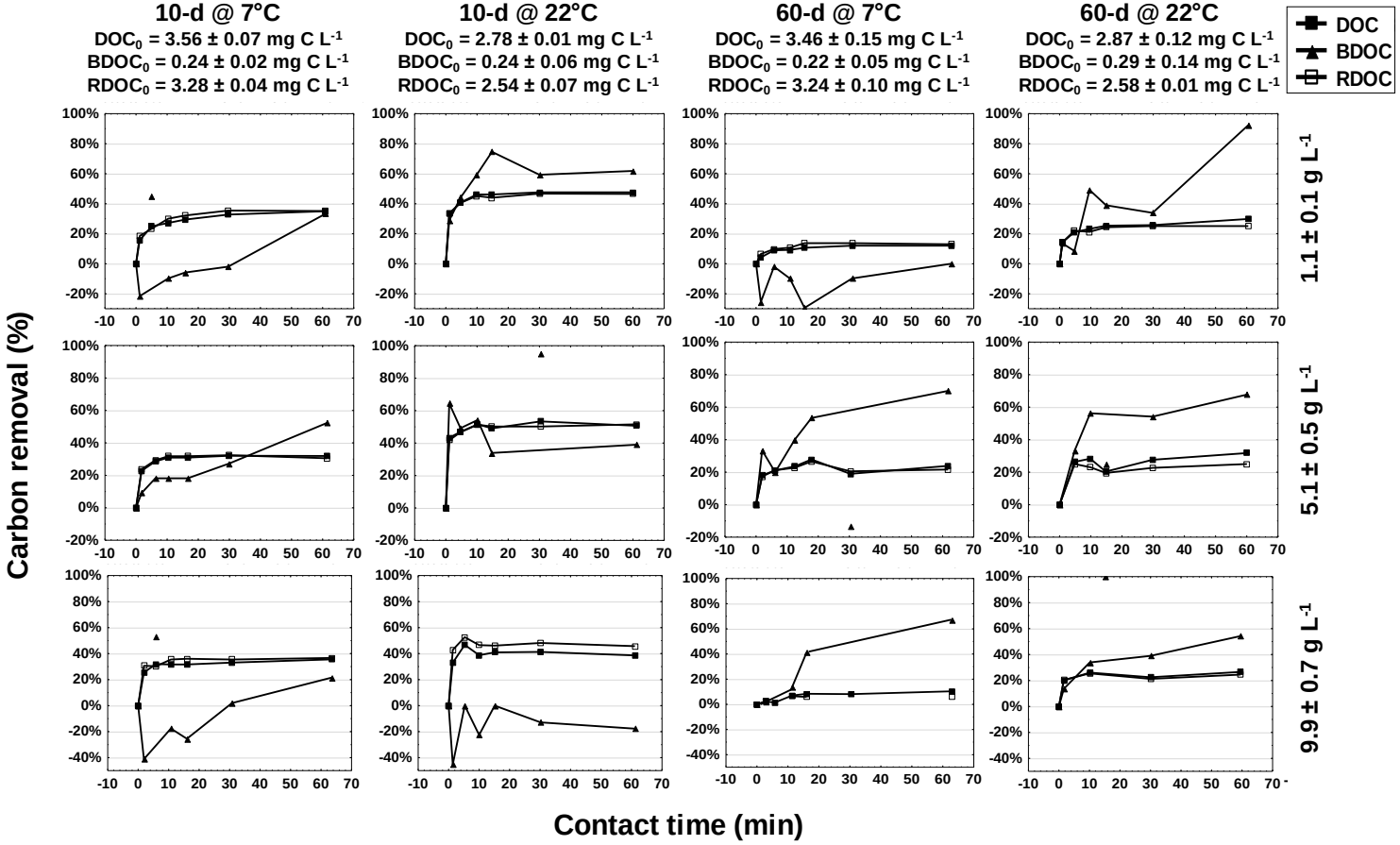

Figure A-3. 2 : DOC, BDOC and RDOC removal kinetics (in %) on 10-d and 60-d PAC at 7°C and 22°C in SW. PAC concentrations were 1.1, 5.1 and 9.9 g L^{-1}.

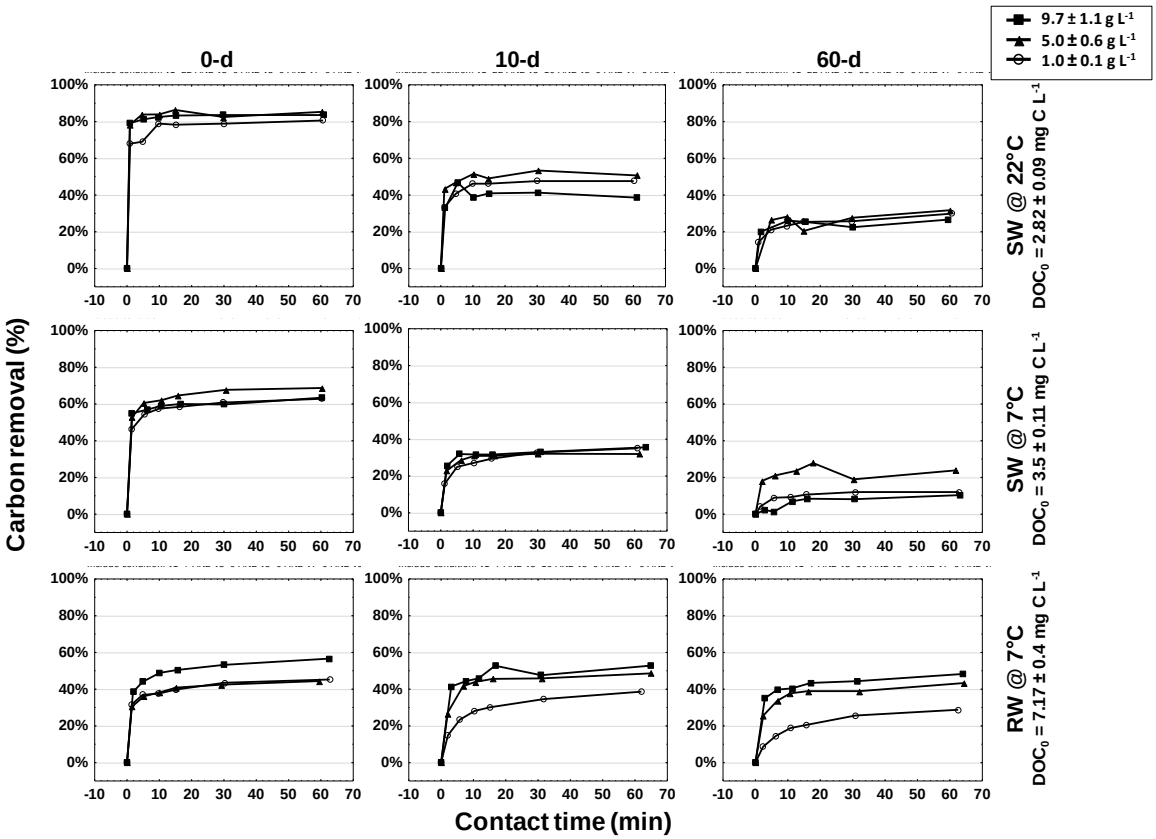

Figure A-3. 3 : DOC removal kinetics (in %) on 0-d, 10-d and 60-d PAC. PAC concentrations were 1.0, 5.0 and 9.7 g L^{-1} in SW at 7 and 22°C and in RW at 7°C.

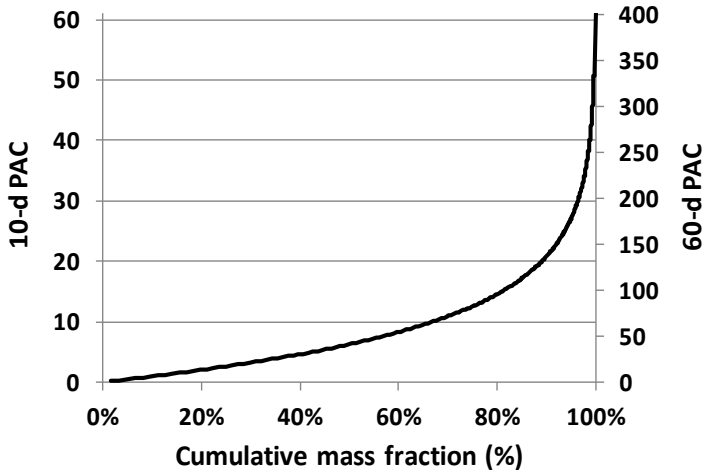

Figure A-3. 4 : Cumulative mass fractions of 10-d and 60-d age distributions.

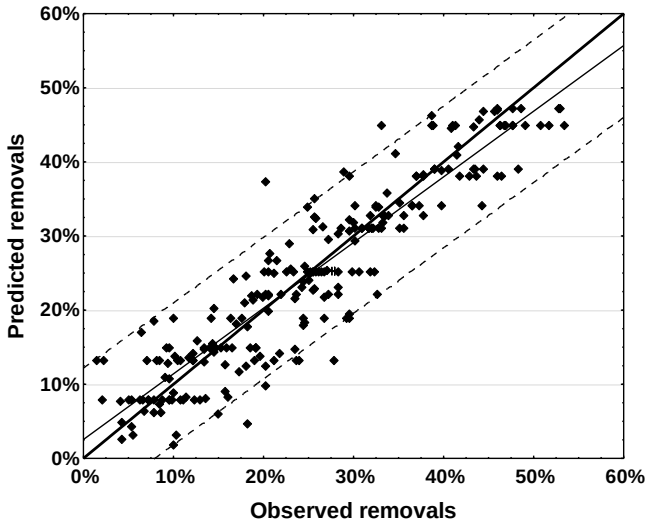

Figure A-3. 5 : Predicted versus observed DOC removals for all the operating conditions computed. The equation of the regression line is y = 0.03 + 0.89*x. Dotted lines correspond to the prediction interval at 95% confidence. As seen in Fig. A-3.5, predicted data are always within a 10% range of the observed percent removals

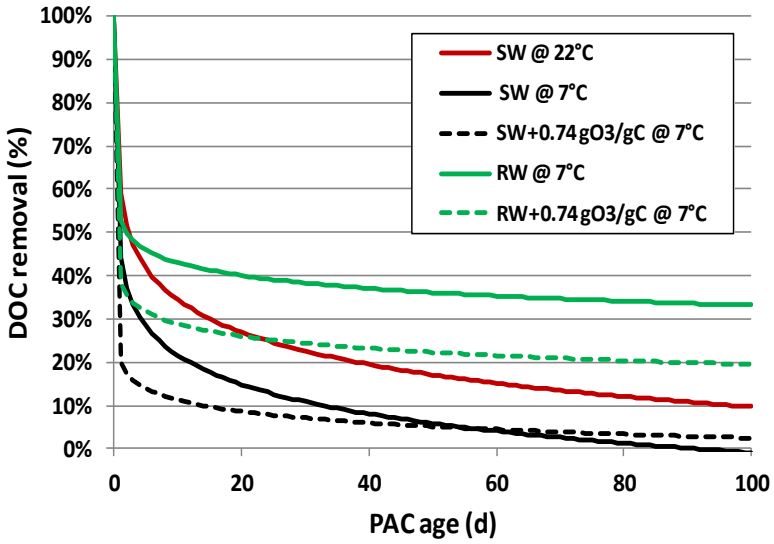

Figure A-3. 6 : Predicted DOC removal (%) for PAC presenting a homogenous age from 0-d to 100-d. The PAC concentration was set to 10 g L^{-1} and the HRT to 30 minutes